THE PRACTICAL CHEMISTRY OF COAL AND ITS PRODUCTS

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To

THE MEMORY OF

THE LATE PROFESSOR L. T. O'SHEA

IN APPRECIATION OF

MANY ACTS OF KINDNESS

PREFACE

THE present work embodies, with some additions, the laboratory course in Fuel Technology at Sheffield University. It is hoped that it may prove useful to chemists engaged at Gas Works and Coke Ovens. We have usually limited ourselves to the description of one reliable method for each determination, and have assumed an elementary knowledge of chemical manipulation on the part of the reader.

Our special thanks are due to H. G. Colman and D. Northall-Laurie for the loan of curves for the estimation of benzene and toluene; to the publishers of the *Gas Journal*, *The Analyst*, and the *Journal of the Society of Chemical Industry*, for permission to reproduce these curves, and other matter; to Messrs. Baird & Tatlock, for the loan of blocks for three diagrams; and to A. E. Beet, who has prepared all the other illustrations.

References to some of the more recent papers will be found in the text. We are also indebted to the following standard works, to which the reader may refer for further information :—

Lunge: *Coal Tar and Ammonia*, *Sulphuric Acid and Alkali*, and *Technical Methods of Chemical Analysis;* Thresh: *Examination of Waters and Water Supplies;* Sutton: *Volumetric Analysis;* Mellor: *Quantitative Analysis;* Redwood: *Petroleum and its Products;* Burgess and Le Chatelier: *Measurement of High Temperatures;* Hempel: *Gas Analysis;* and Haldane: *Air Analysis.*

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CHAPTER I

COAL AND COKE

SAMPLING

VERY great care must be taken in sampling a large quantity of coal in order to get a really representative sample. The errors due to bad sampling are usually very much greater than those incidental to chemical analysis.

The original sample must be at least 1 per cent. of the main bulk, and must be so collected that it fairly represents the bulk. Trucks, storage hoppers and the like should be sampled during loading or unloading, a portion being set aside at intervals in a weatherproof sampling bin. Similarly samples of coking slacks before washing can be taken from the conveyors and after washing from the top of the washer. To sample a seam of coal a clean cut is made from top to bottom of a newly-exposed face, about 2 ft. wide and 2 ft. deep; this should be loaded into a truck and labelled so that it cannot go astray at the surface.

The original sample must be reduced to about 2 lb. (1 kilo) by a process of repeated breaking up, mixing and quartering. The degree of sub-division necessary at each stage before quartering is given in the following table (*see* E. G. Bailey, *J. Ind. Eng. Chem.*, 1909, **1**, 161):

Weight of Coal.	Size of Sieve.
7,500 lb.	2 in.
1,200 lb.	1 in.
180 lb.	$\frac{1}{2}$ in.
5 lb.	$\frac{1}{4}$ in.
2 lb.	$\frac{1}{8}$ in.

Quartering is effected by building, on a clean dry concrete floor, a uniform conical heap of coal, each additional shovelful being thrown directly on top of the cone. When complete the cone is flattened into a "pancake" by shovelling round and round outwards from the centre. This is then carefully divided into quarters by two cuts at right angles and opposite quarters are rejected, the weight of the sample being thus halved. This process is repeated as often as necessary, the coal being broken up and sifted as indicated by the table.

The 2 lb. sample is placed in an air-tight bottle, labelled and dated, and sent to the laboratory for analysis. In the laboratory the whole sample is ground to pass a 30-mesh sieve and well mixed. Two test-tubes full of this, further ground to pass a 90-mesh sieve, will suffice for an ordinary analysis. All determinations should be duplicated. Equal care should be taken in sampling any product for analysis.

MOISTURE

If the sample of coal is very wet it must be air-dried before grinding. About a kilogramme of the wet coal is weighed out on a shallow tray, and left in a warm room till dry. It is then reweighed, after which it may be ground up for analysis. The moisture so found must be added to that obtained by further drying.

To estimate the moisture in the ground sample a pair of watch-glasses clipped together so as to form a lenticular receptacle is used. The glasses are dried at 105° C., cooled in a desiccator and weighed. About a gramme of the sample is placed in the lower glass, which is immediately covered with the other. The whole is then weighed, and the clip placed in position. The upper glass is drawn aside a little so as to allow evaporation, and the whole dried in the oven at 105° C. for one hour, after which it is cooled, unclipped and weighed as before. A further half-hour's drying is then given, and the glasses again weighed, and so on, as long as

any decrease in weight takes place. Usually the weight increases slightly after a time, owing to incipient oxidation. The lowest weighing is taken as giving the weight of dry coal. Oxidation does not take place with coke.

Dry coal will usually reabsorb a little moisture if left for some days in a desiccator: hence, if left, the coal should always be dried a further half-hour before weighing. Care should be taken to finger the glasses as little as possible.

ASH

A recently ignited silica (or preferably platinum) basin is weighed: about a gramme of coal is placed in it, and the basin and coal weighed. It is placed on the ledge in front of the muffle and left until the volatile matter is (slowly) driven off. The basin is then placed in the furnace, which should be at a bright red heat; coke may be placed in the furnace without the preliminary heating. After an hour's heating the basin is withdrawn and while held with the tongs the contents are very carefully stirred with a glass rod; if no unburnt particles can be seen the rod is brushed into the basin, which is allowed to cool in a desiccator and weighed, after which it should be replaced in the muffle for about fifteen minutes to make sure that the combustion is complete. Note the colour of the ash.

It should be noted that there is usually a partial vacuum in the desiccator owing to the great heat of the basin when put in. The desiccator must therefore be opened gradually or the ash will be blown about. It is an advantage to use a vacuum desiccator, admitting air slowly through the tap before opening.

MINE ROAD DUST

To determine the combustible matter in a mine dust sample this is first sifted through the gauze cap of an ordinary safety lamp, all that will not pass the screen being rejected. The moisture and ash are then determined as above, and the combustible matter obtained by difference.

Very wet samples must be dried before sifting. If lime-

stone has been used for stone-dusting purposes the carbon dioxide present in it, which is expelled by incineration, will be included in the combustible matter. It is therefore necessary in such cases to determine the carbon dioxide present. This is easily done by treating the dust with acid in a Schrötter apparatus, and noting the loss in weight.

VOLATILE MATTER (Coal)

A platinum crucible is heated in the muffle, cooled and weighed. About 1·5 grammes of coal are placed in it and it is re-weighed. A special burner giving an extra large flame, barely non-luminous, is used. The crucible is supported on a pipe-clay triangle about 3 in. from the top of the burner, so that it is completely enveloped in flame. The volatile matter is expelled from the coal and burns with a luminous flame. Heating is continued for exactly one minute after the luminosity of the flame dies down; and the flame is then removed and the crucible heated for a further minute over the blow-pipe (which must be in readiness). All soot on the outside of the crucible lid should burn off; the crucible is then allowed to cool, and weighed. The loss of weight gives the weight of volatile matter, including moisture, which should be deducted. The weight of the residual coke, minus the weight of ash, gives the weight of fixed carbon. Note the coherence or otherwise of the coke.

See also Lessing's method (*J.S.C.I.* 1912, **31**, 465 and 671).

VOLATILE MATTER (Coke)

A small porcelain crucible and lid are burnt clean, cooled and weighed. One or two grammes of finely ground coke are added and the whole re-weighed. A few drops of benzene are then added and the crucible covered. It is placed inside a larger crucible, the space between being packed with small pieces of coke, so that the small crucible is quite buried. Place the lid on the outer crucible and ignite in the muffle at a bright red heat for half an hour; then remove and cool in a desiccator. The benzene creates

a neutral atmosphere inside the small crucible, and on cooling air is drawn in through the glowing coke, the oxygen being thus converted to carbon-dioxide, so that the coke in the inner crucible is not oxidised.

When cool the inner crucible and lid are withdrawn, brushed clean, and re-weighed, great care being taken not to introduce any coke from the larger crucible. The loss in weight gives the weight of volatile matter in the coke, including moisture, which must be deducted.

SULPHUR (Eschka's method)

(*See also* the chapter on ash analysis.)

One gramme of coal is required for this determination. Three grammes of special fusion mixture (3 parts magnesia, 1 part anhydrous sodium carbonate) is weighed out. The bulk of it is brushed into a platinum basin, where it is carefully mixed with the coal by stirring with a dry glass rod, which is afterwards brushed clean: the rest of the fusion mixture (about 0·5 gramme) is carefully brushed over the surface to form a thin white layer. Do not tap the mixture down level after stirring, as this makes the particles settle closely together and retards the oxidation.

The basin is now heated gently for half an hour over a small flame the size of a hazel nut, placed two inches below the basin. Part of the volatile matter is thereby slowly expelled, and no smell of sulphuretted hydrogen should be noticed during the operation. The basin is then transferred to a muffle furnace heated at dull redness and allowed to remain till all the carbon seems burnt off (about 1 hour); the contents are then carefully stirred with a glass rod, and if unburnt particles are seen, further heating is given.

When cool, transfer the contents of the basin to a beaker with the help of about 50 c.c. of distilled water. Add 10 c.c. of bromine water and cover with a clock glass. Measure 30 c.c. of concentrated hydrochloric acid (in the measuring cylinder still wet with bromine water) and add it to the beaker a little at a time, allowing the effervescence

to subside between each addition. The basin should be rinsed out with some of the acid. All the fusion mixture is dissolved and the bromine oxidises all sulphur compounds to sulphate. Boil the solution to remove the excess of bromine, and filter the hot solution from the small quantity of sandy residue, which must be washed with hot distilled water as long as the washings redden blue litmus paper. If there are any black particles in the residue the coal is not completely burnt off, and the experiment should be repeated.

Boil the filtrate and washings, and add, with constant stirring, 10 c.c. of 10 per cent. barium chloride solution, drop by drop. The filtrate should occupy at least 250 c.c. before the barium chloride is added. Boil for 10 minutes and allow the precipitate to settle out overnight.

Decant the clear liquid through a filter-paper and wash the precipitate several times by decantation with hot water; then transfer it to the filter with the help of the wash bottle and a rubber-tipped glass rod, and wash it further until the washings show no cloudiness when tested with silver nitrate solution.

Transfer the filter to a weighed crucible, ignite it in the muffle till the paper is completely burnt, and weigh: 0·1374 times the weight of barium sulphate gives the weight of sulphur ($0{\cdot}1374 = \frac{11}{80}$ approximately).

It is necessary to subtract from the weight of barium sulphate that due to the sulphur in the fusion mixture. This is found, for each new batch of fusion mixture, by a blank experiment in which 3 grammes of fusion mixture, without coal, is treated exactly as in the determination.

For the best results an electrically heated muffle furnace should be used to avoid introducing sulphur from the gas of a gas muffle.

ARSENIC

Fifty grammes of coal or coke are digested with aqua regia on a water-bath for several hours, adding more acid as required. The acid is then diluted with hot water and

filtered through a large filter-paper, the residue being washed with boiling water. The filtrate and washings are treated with 2 c.c. of 30 per cent. ferric chloride solution, and excess of ammonia added: the arsenic is precipitated with the iron.

The precipitate is washed and dissolved in hydrochloric acid, and distilled in a 4 oz. retort with the addition of 5 c.c. of ferrous chloride solution, 5 c.c. of water, and 20 c.c. of hydrochloric acid. The retort is placed with its neck inclined upwards at 45°, the end being bent downwards and connected to a vertical worm condenser. To the residue in the retort add 20 c.c. of hydrochloric acid and 5 c.c. of water and again distil; repeat this twice more, adding also 5 c.c. of ferrous chloride solution to the third (but not the fourth) residue.

The distillate is neutralised with ammonia, slightly acidified with hydrochloric acid and cooled under the tap. It is then made alkaline with sodium bicarbonate and titrated with iodine solution, using starch as indicator. The iodine solution contains 1·693 grammes of iodine and 2 grammes of potassium iodine per litre; 1 c.c. = 0·0005 gramme arsenic. It is standardised against a standard sodium arsenite solution, containing 0·66 grammes of arsenious oxide (*i.e.* 0·5 gramme arsenic) and 2 grammes of sodium carbonate, which are boiled with 100 c.c. of water till dissolved: it is cooled, 2 grammes of sodium bicarbonate added, and made up to 1 litre.

The ferrous chloride solution is made by dissolving 10 grammes of iron in dilute hydrochloric acid and diluting to 100 c.c. A blank test should be done with the reagents used.

[*See also* Archbutt and Jackson, *J.S.C.I.* 1901, p. 449, and Thorpe, *J.C.S.* 1903, p. 969.]

NITROGEN (Kjeldahl's method)

One gramme of coal and 5 grammes of potassium bisulphate are introduced into a long-necked round-bottomed glass flask and 15 c.c. of concentrated sulphuric acid added. Loosely close the mouth of the flask with a small glass

bulb, and gently heat the acid over a small flame until all the coal is dissolved to a clear solution. The neck of the flask should be slightly inclined to facilitate condensation of the acid. When cold the contents of the flask are diluted with distilled water, and poured into an ammonia distillation apparatus (*see* the Section on AMMONIA). Add a little phenolphthalein solution, then run in from the dropping funnel saturated caustic soda solution until quite alkaline (permanent red colour). Distil the ammonia into 25 c.c. of $\frac{N}{10}$ acid, and titrate the excess with $\frac{N}{10}$ alkali. The difference is the acid equivalent to the ammonia: 1 c.c. $\frac{N}{10}$ acid $= 0{\cdot}0014$ gramme nitrogen. The solution in the distillation flask should not be too concentrated; it should be diluted to about 300 c.c. before distilling.

A blank experiment should be made on 1 gramme of cane sugar. Usually less than 0·5 c.c. $\frac{N}{10}$ acid will be required for this. It is rather better to use fuming sulphuric acid, which is free from nitrogen compounds, as it is invariably made by the contact process.

The solution of the coal is greatly hastened by adding a small globule of mercury to the flask: in this case, however, sodium sulphide solution sufficient to precipitate all the mercury must be added before distilling.

A copper flask is often recommended for the distillation but is quite unnecessary. An ordinary flat-bottomed (glass) flask in our laboratory has already withstood several dozen distillations, besides many ordinary ammonia distillations.

(Dumas' method may also be used. In this case the nitrogen collected should be tested for methane.)

DIRT (in Coking Slack)

The dirt should be estimated both before and after the washing process in order to determine the percentage of dirt removed by the washer.

One kilogramme of dry coal is weighed out; it is then screened through 1 in., $\frac{1}{2}$ in., $\frac{1}{4}$ in., $\frac{1}{8}$ in., and $\frac{1}{16}$ in. sieves, and the weights of each fraction recorded, together with the loss in sifting. Sizing the coal in this way greatly assists the subsequent separation.

Each fraction (starting with the largest) is then separated by the use of a solution of zinc or calcium chloride of specific gravity 1·4 (tested by a hydrometer). This is contained in a beaker. The coal is added a little at a time, taking care that it is thoroughly wetted.

All that sinks is regarded as dirt. The floating pieces are removed from time to time with a bent spoon or crucible tongs, and thrown away to make room for more coal.

When the fraction is all separated the solution is decanted from the dirt, which is then washed by running a stream of water from the tap into the beaker, care being taken that no pieces are washed over.

The dirt is then dried and weighed. The whole of the larger coal must be separated, but it is sufficient to treat a part only of the smaller coal. The following table indicates the minimum weights to be taken in each case:—

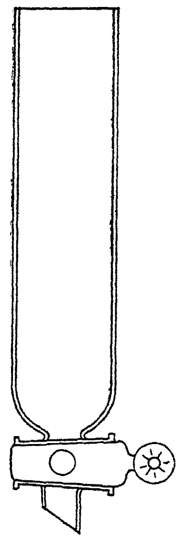

FIG. 1.—SEPARATING FUNNEL FOR DIRT ESTIMATION.

Under $\frac{1}{16}$ in.	10 grammes.
$\frac{1}{16}$ in. to $\frac{1}{8}$ in.	50 ,,
$\frac{1}{8}$ in. to $\frac{1}{4}$ in.	200 ,,

The finest coal is best separated by use of a special separating funnel (FIG. 1) with a wide-bore tap, through which the dirt may be run with some of the liquid. The dirt is collected on a Buchner funnel and washed with hot water. If zinc chloride be used, the first washing should be with dilute hydrochloric acid, to prevent precipitation of basic zinc chloride; this need not be done with the larger lumps, as the precipitate is easily rinsed away.

From the amount of dirt in each fraction the weight of dirt in the original sample is readily calculated.

Instead of salt solutions, chloroform, diluted with alcohol or ether, may be employed for the separation. This is very mobile and readily wets the coal, and the dirt requires no washing and is quickly dried. Care however is needed to prevent excessive loss of chloroform by evaporation (*see* Blyth and O'Shea, *Tr. Inst. Min. Eng.*, **LVII**, pt. 5, 261).

In connection with the above the specific gravity of selected pieces of the clean coal may be found by the use of a specific gravity bottle. This is first weighed full of water and then emptied, a known weight of coal being placed inside, and the bottle about half filled with water. Air bubbles are removed from the submerged coal by connecting the bottle to the filter pump, and warming the bottle in hot water so as to boil the contents. After cooling, the bottle is filled and weighed. The following example shows the method of calculation :—

Wt. of coal	= 1·072 grammes	} total = 62·191 grammes.
Wt. of bottle + water	= 61·119 ,,	
Wt. of bottle + coal + water	= 61·333 ,,	
Wt. of water displaced by coal	= 62·191 ,, − 61·333 grammes = ·858 grammes.	

$$\text{S. G. of coal} = \frac{1{\cdot}072}{{\cdot}858} = 1{\cdot}25.$$

COKING POWER

For this test 1 gramme of ground coal is mixed in succession with 1, 2, 3, &c. grammes of inert material, and the volatiles expelled as previously described under volatile matter. The greatest weight of inert material with which the coke is just coherent gives the "coking index."

Calais sand was the inert material originally employed by Campredon and it has the advantage of being ready for use. More consistent results are obtained (according to Sinatt, *J.S.C.I.* 1920, **39**, 83) by the use of electrode carbon screened between 60 and 90 mesh (or better between 80

and 90 mesh). This material is very hard to grind, but may readily be reduced by wrapping in cloth and hammering. The coal should be ground to pass a 90-mesh sieve. The coherence of the coke is tested by placing the button under a 100-gramme weight of the same diameter. We have found some trouble with this method owing to partial coking giving perhaps a semicircular button with a 50 per cent. yield of non-adherent powder.

For comparative results a uniform procedure is essential.

POROSITY OF COKE

This involves the determination of the real and apparent specific gravities of the coke.

The real specific gravity is determined by the use of finely ground coke in a specific gravity bottle, exactly as described under coal. Special care must be taken to remove air-bubbles from the submerged coke.

For the apparent specific gravity a fairly large piece of coke is suspended by a fine thread from the hook of a balance-pan and weighed

(1) In air.

(2) In water (contained in a small beaker standing on a wooden bridge over the pan).

The difference in the two weighings gives the weight of water displaced by the coke ; the weight of coke divided by the weight of water it displaces gives the apparent specific gravity.

The weighing in water should be conducted as rapidly as possible to prevent the water from displacing the air from the pores of the coke.

The percentage porosity is then given by the formula

$$\frac{\text{Real S. G.} - \text{apparent S. G.}}{\text{Real S. G.}} \times 100$$

N.B.—The pores of the coke are in reality not filled with air but residual coal-gas, chiefly hydrogen and carbon monoxide.

HARDNESS OF COKE

A piece of coke is ground into a centimetre cube (or other convenient size) and its crushing strength determined by means of a lever testing machine.

DISTILLATION (High Temperature)

A special combustion tube, closed at one end, length 60 cm., internal diameter 13 mm., wall thickness 2 mm., is used (FIG. 2). Fifteen grammes of coal is placed in it, with a small ignited asbestos plug to keep it in position; 10 cm. of burnt fire-clay lumps (the size of small peas) are then added, and another asbestos plug. The tube is then weighed and about 17 cm. of dry cotton-wool placed at the front end. It is then re-weighed, the difference giving the weight of cotton-wool, which acts as a tar-scrubber.

The following (weighed) absorption vessels are connected to the tube by a rubber cork.

(1) Bulb of dilute sulphuric acid; Calcium chloride tube.

(2) Bulb of strong potash solution (1 : 1); calcium chloride tube.

(3) Two bulbs of creosote oil; calcium chloride tube.

The tubes are connected through a calcium chloride guard tube to a water aspirator (gas-holder) having a syphon outlet of such length as to give a suction of 60 mm. of mercury. The tightness of the joints is tested by turning the suction full on. All air is next displaced from the holder. In order to keep the rest of the apparatus exhausted it is cut off from the holder by means of a tap or screw-clip during this operation.

The tube is heated in a combustion furnace, the cotton-wool part being maintained at 100° C. in a steam bath. To start the distillation the latter is heated and the firebrick raised to a red heat (this takes about fifteen minutes, with a gas pressure of 20 mm.). A burner is then turned on full every ten minutes, working from the firebrick to the closed end. When gas ceases to be evolved the gas holder is cut off by a clip or tap, and its contents adjusted to atmospheric

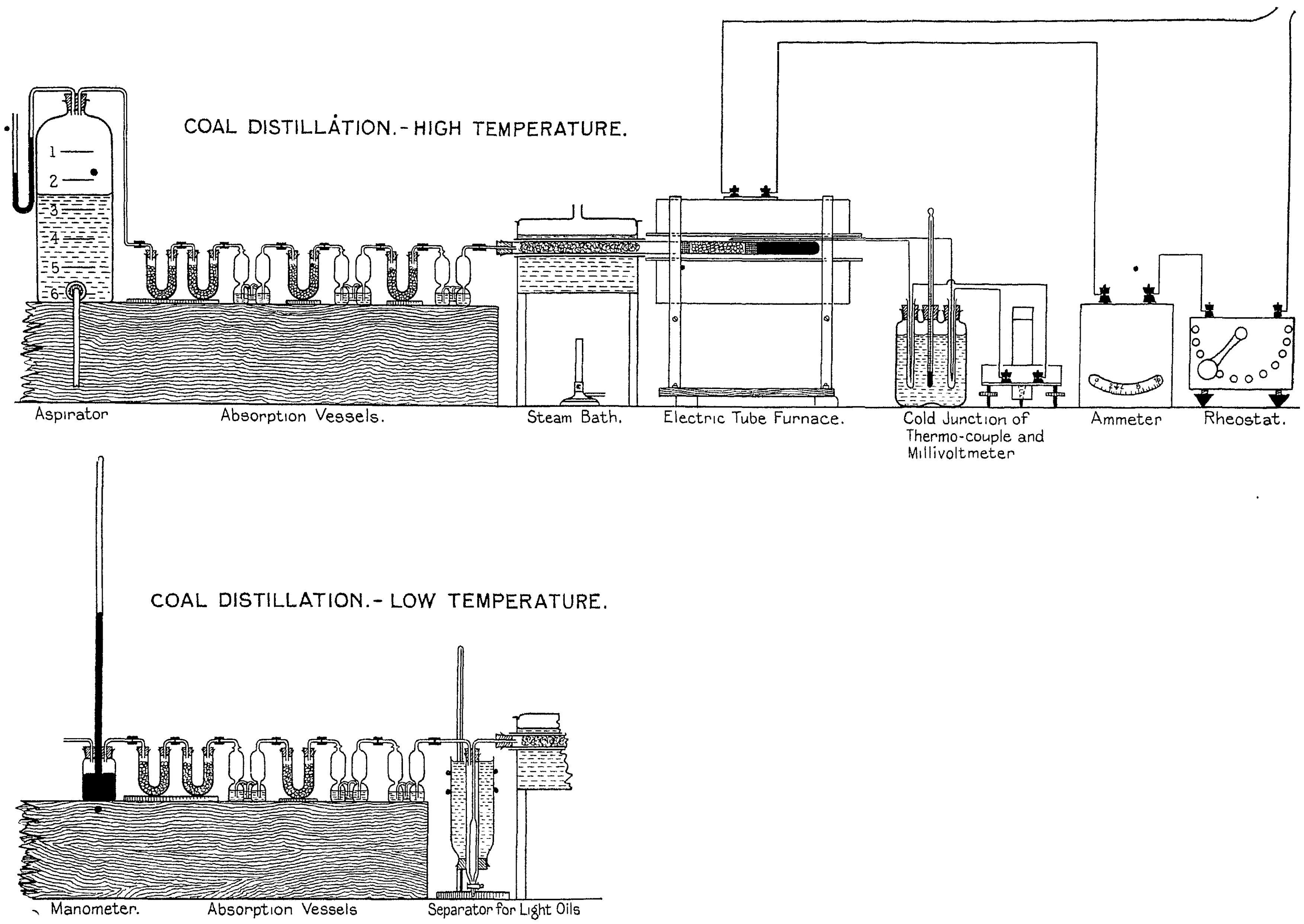

FIG. 2.—HIGH AND LOW TEMPERATURE DISTILLATION APPARATUS

pressure and measured. The furnace is meanwhile extinguished and the cork carefully withdrawn from the combustion tube. A gas sample is then taken. After this the holder is again put into communication with the bulbs and dry air drawn through to displace the gas in the bulbs. These are then re-weighed. The increases in weight give:—

(1) Ammoniacal liquor.
(2) $CO_2 + H_2S$.
(3) Benzol.

The ammonia in (1) is estimated by distillation into 30 c.c. of $\frac{N}{10}$ acid (*see* AMMONIA, p. 40). The H_2S in (2) is estimated by making up the potash solution to 100 c.c., and taking 10 c.c.; to this 10 c.c. of $\frac{N}{10}$ iodine solution is added, and then acetic acid to make the whole acid. The excess of iodine is titrated with $\frac{N}{10}$ sodium thiosulphate, and the difference is the iodine used by the sulphuretted hydrogen according to the equation

$$H_2S + I_2 = 2HI + S,$$

so that each c.c. of $\frac{N}{10}$ iodine re-acts with 0·0017 grammes H_2S. (*See* page 36 for preparation of solutions.)

The loss in weight of the combustion tube gives volatile matter minus tar. The tar is estimated by cutting off the cotton-wool piece and weighing it. The ammonium salts ("fixed ammonia") are washed out with hot water and estimated by distillation into 10 c.c. of $\frac{N}{10}$ acid. The cotton-wool is removed and the tar-piece cleaned, dried, and weighed. The difference in the weighings gives cotton-wool + tar. The coke is estimated by difference and may be weighed directly as a check.

To complete the test the coke and gas are analysed. The gas analysis is corrected for the air contained (equal in

volume to the gas remaining in the absorption tubes) by subtracting the oxygen found and the corresponding amount of nitrogen. The following factors are useful in calculation :—

Per cent. coke $\times$ 0·2 = cwts. per ton of coal.

Per cent. NH_3 $\times$ 86·94 = lb. $(NH_4)_2SO_4$ per ton.

Per cent tar $\times$ 2·0 = galls. per ton.

Per cent. liquor $\times$ 2·20 = galls. per ton.

Cu. metres per kilo. $\times$ 35,880 = cu. feet per ton.

The volume of gas is calculated :—

(1) At N.T.P., dry, in cubic feet per ton.

(2) Ditto, including CO_2, H_2S and benzol, by multiplying the respective percentages by 182, 236. 95, and adding them to (1).

(3) At 15° C., wet, N.P. by multiplying by 1·073.

DISTILLATION (Modified for Low Temperature)

The tube is similarly packed, the plugs used being prepared by rolling up together a compound strip, 1 cm. wide, of wire-gauze and asbestos, the former being outside; these plugs are not liable to become choked and blown along the tube. The tube is then heated in a small electric tube furnace maintained at 600° C. (tested by a thermocouple). At the beginning of the experiment the closed end of the tube, with the coal, entirely projects from the end of the hot tube furnace. The tube is moved at intervals parallel to its axis so that successive portions of the coal are distilled, finishing at the closed end, the furnace being maintained in each position, until gas ceases to be evolved.

Before passing into the absorption apparatus the gas passes through a special separator (which is water-jacketed) consisting of a short burette graduated right down to the glass stop-cock, which is outside the water jacket. The gas is led down to the bottom of this vessel by a tube, which is pipette-shaped to provide against sucking back. Here most of the oil not retained by the cotton-wool, and

most of the ammonia liquor, condenses, and the volumes of each are read off at the end of the experiment, after raising the inlet tube and allowing it to drain. The ammonia liquor, after measuring, is rinsed out (into the distillation flask) before measuring the oil: this allows the oil (about 0·2 c.c.) to be measured in the narrowest part of the tube. The mean density of the oil (light and heavy) may be taken as unity. The potash bulb and the gas holder are omitted and the creosote bulb connected through a closed manometer to a filter pump, the gas being estimated roughly by difference. (*See* Beet and Findley, *Tr. Inst. Min. Eng.*, **LX**, pt. 3, 213.)

N.B.—A tube furnace at 900° C. may be used for the high temperature distillation.

CARBON AND HYDROGEN

For this purpose a combustion tube about 90 cm. long and 2 cm. in diameter is required. The best way to cut the tube is to file a deep groove round it, then place two bands of wet filter paper round the tube, one on each side of the groove, about 0·25 cm. apart. The groove is heated in a fish-tail flame, placed with its edge along the groove, until cracking takes place. Do not rotate the tube in the flame nor bring it slowly into the flame. The cut ends are then ground fairly smooth by the use of a piece of wet grindstone. It is advisable to anneal the tube before proceeding further, and the tube is therefore placed in the combustion furnace and all the burners lighted as low as possible (the air being reduced to prevent striking back). After half an hour the tube is covered over with the tiles and left a further half-hour; the burners may then be turned on sufficiently to maintain a dull red heat. After an hour or two the burners are again turned low and alternate burners are then extinguished at half-hourly intervals until only three or four remain alight. Finally extinguish these and allow the tube to cool in the furnace overnight. The same method of heating and cooling the tube should always be adopted The tube is then packed as indicated

in the diagram (FIG. 2). The spirals are made by tightly wrapping copper gauze round thick copper wire which must have a loop at one end to allow the spiral to be withdrawn by means of a hooked wire. The spirals are ignited in the blow-pipe; the one near the entry is placed in a desiccator and re-ignited just before use. The reduced spiral is obtained by dropping the hot spiral into a test tube containing 1 c.c. of methyl alcohol. As the flame dies down a crucible lid is placed over the tube, and when cold the spiral is turned out on to a clock glass and left in the steam oven till free from methyl alcohol.

Silvered pumice is made by dipping pumice soaked in water into powdered silver nitrate and igniting in a muffle until nitrous fumes cease to be evolved; it has a white surface which, if rubbed on glass, acquires a bright metallic silver lustre. The copper oxide should be that made by calcining wire. The lead chromate should pass a $\frac{1}{4}$-inch sieve and rest on $\frac{1}{16}$ inch: it is contained in a cartridge of asbestos paper, made by moistening the paper and rolling it round a glass tube of suitable diameter. When dry it is filled, plugged with asbestos and carefully inserted. It must fit closely.

Two gas holders containing air and oxygen respectively are required. The holder containing air can be advantageously replaced by a small blower of the filter-pump type, attached to a water-tap. The gases are delivered into the tube through a duplicate purifying set, comprising :—

(1) Two wash-bottles containing strong potash solution (equal weights of water and potash).

(2) A large U-tube containing calcium chloride.

(3) A small "bubbler" containing a few c.c. of concentrated sulphuric acid (renewed for each experiment).

The tube must be "burnt out" by heating in a stream of air. Take care not to overheat the tube: the lead chromate part should never be visibly red hot, and for the rest a dull red heat is enough. Remove water from the outlet end with filter paper as it condenses. Two days or

more may be needed to burn off all the "dressing" from the asbestos paper. Trial combustions should then be made with pure filter-paper (dried at 105°C.) as described below until correct results are obtained, indicating that the tube is thoroughly burnt out and the manipulation mastered. The reduced spiral is not required in these combustions. The absorption vessels used are :—

(1) A U-tube containing granular calcium chloride. This is provided with a bulb at the entry, in which most of the water condenses, and may be emptied out after each combustion. The calcium chloride should be saturated with carbon dioxide by passing a slow stream of the dried gas through it for two hours. The tube is then plugged and allowed to remain full of carbon dioxide overnight, after which that gas is displaced by dry air, free from carbon dioxide. This tube serves for many combustions.

(2) Two potash bulbs charged with the strong potash solution: the second is provided with an exit calcium chloride tube. The first bulb is re-charged for each combustion.

The absorption vessels are plugged and their surfaces wiped with a clean dry cloth. After standing an hour in the balance case they may be weighed, minus the plugs. The weighing is best done against a similar set of vessels which serve as counterpoises. Errors due to variations in density of air displaced, and amount of moisture condensed on

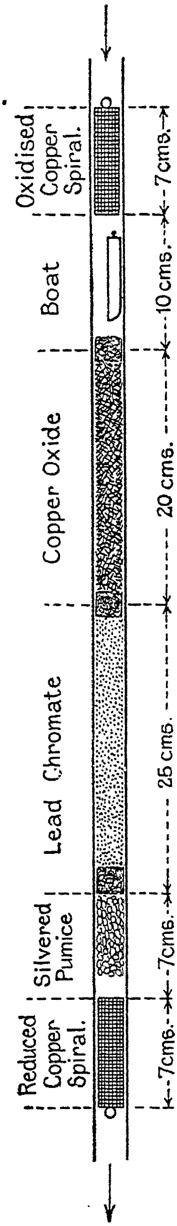

FIG. 3.—METHOD OF PACKING COMBUSTION TUBE.

the surfaces, are thus eliminated. After weighing, the vessels are re-plugged until wanted.

About 0·25 grammes of coal, dried at 105° C. for one hour, is weighed out in a weighed (dry) porcelain or platinum boat, enclosed in a weighing tube. The combustion tube should meanwhile have been heated up, and then the empty part left for the boat and the oxidised spiral, together with the reduced spiral space, allowed to cool.

The reduced spiral is placed in position and the tube closed by a rubber cork through which one end of the calcium chloride tube passes. The potash bulbs are then connected on with short pieces of rubber tubing, making "glass-to-glass" joints. Do not moisten the tubes to facilitate joining. Take care that the bulbs are right way round.

The other end of the tube is then opened and the boat and oxidised spiral inserted. Everything should be at hand before opening the tube, so as to minimise admission of moist air. No organic matter must be introduced by "fingering."

A stream of oxygen is then passed through the tube and adjusted so that the bubbler gives about two bubbles a second—at this rate a molecule of gas takes about 5 minutes to traverse the tube. Note carefully if the bubbling through the absorption bulbs corresponds, as this indicates whether the apparatus is gas-tight.

The oxidised spiral at the entry is then raised to a dull red heat, after which the burners under the boat may be lighted one at a time, so as to distil off the volatile matter as slowly as possible. At the same time the burners under the reduced spiral are lighted, but care is required to avoid premature oxidation of this spiral.

The start of the combustion is indicated by condensation of water about the exit of the tube ; at the same time the bubbling in the absorption vessels slackens, the first compartment of the potash bulbs being much more rapid than the rest. The oxygen will probably have to be turned on a little to keep the bubbler working at the required speed.

If it goes too slowly there is danger of the products diffusing backwards into the purifying vessels. The exit end of the tube should be kept free from condensed moisture by warming with a hot tile from the furnace if necessary.

When all the volatile matter is driven off the boat is heated more strongly until the coke begins to glow. If the coal was evenly distributed in the boat the coke will now burn off steadily. The end of the combustion is indicated quite sharply by the glow ceasing. The oxygen is passed until the exit gases will re-kindle a glowing splint, after which air is substituted until all the oxygen is swept out. While this is going on the tube may be cooled ready for the next combustion, or for leaving. The actual combustion takes about two hours.

The absorption vessels are detached, plugged, wiped, allowed to stand in the balance case one hour, and weighed. The boat containing the ash is also carefully withdrawn and weighed. The ash should not lose weight on subsequent ignition in the muffle. After weighing the condensed water is tested with litmus paper. It should not be acid.

$\frac{3}{11}$ of the weight of carbon dioxide (absorbed in the potash bulbs) gives the carbon, and $\frac{1}{9}$ of the water (in the calcium chloride tube) the hydrogen.

Phosphorus. See Chapter VII on Ash Analysis.

CHAPTER II

PURIFYING MATERIALS, ETC.

PREPARATION OF NORMAL SULPHURIC ACID

27·5 c.c. of concentrated sulphuric acid are run slowly from a burette into a litre measuring flask half full of distilled water: after cooling, more water is added to give a litre of solution. The solution is well shaken and transferred to a stoppered bottle. Normal hydrochloric acid may be similarly prepared by diluting 100 c.c. of the concentrated acid to 1 litre.

Acid so prepared must be standardised by the use of sodium carbonate prepared by heating in a porcelain basin over a bunsen flame, with continual stirring to avoid clotting. After about half an hour the sodium carbonate will be dry, and should be allowed to cool in a desiccator.

For use, quantities of 1·325 grammes of sodium carbonate are weighed out and dissolved in distilled water; if many lots are wanted, dissolve 13·25 grammes, dilute the solution to 250 c.c. in a measuring flask, and pipette off quantities of 25 c.c. This quantity of sodium carbonate should exactly neutralise 25 c.c. of normal acid, using methyl orange as indicator (the acid being run in from a burette until the colour changes from yellow to red). If, however, a different quantity is used, it is easy to calculate by multiplication the factor by which any quantity of the acid may be converted into its equivalent of normal acid. Thus, supposing 24·5 c.c. of acid were used, the acid is too strong, and the factor is $\frac{25}{24 \cdot 5} = 1 \cdot 020$. If desired, the strength of this acid could be made exactly normal by diluting every

24·5 c.c. to 25 c.c., or 980 c.c. to 1 litre. Standard solutions that are in constant use, and keep well, should always be adjusted in this manner.

EVALUATION OF LIME BY NORMAL HYDROCHLORIC ACID

Sulphuric acid should not be used for this estimation on account of the sparing solubility of calcium sulphate. The equation :—

$$CaO + 2HCl = CaCl_2 + H_2O$$

shows that 28 grammes of lime react with 36·5 grammes of hydrochloric acid, that is with 1 litre of normal hydrochloric acid, so that each c.c. of acid used represents 0·028 gramme of lime. Accordingly about 0·7 gramme of lime is weighed out for the estimation and then slaked, if necessary, by adding a little water.

Lime is not very soluble in water, but dissolves readily in a solution of cane sugar ; it is therefore stirred up with, say, 25 c.c. of 10 per cent. sugar solution, and the liquid decanted through a filter paper. The residue consists chiefly of calcium carbonate and must be washed first with sugar solution and finally with distilled water. A drop of the final wash water must give no blue colour with red litmus paper. The filtration must be done rapidly, avoiding undue exposure to air. To the filtrate and washings methyl orange is added, and they are then titrated with normal hydrochloric acid.

Decinormal acid $\left(\frac{N}{10}\text{ acid}\right)$ can easily be prepared and standardised, using $\frac{1}{10}$ of the quantity of acid, etc., per litre. A similar remark applies in every case.

PREPARATION OF NORMAL CAUSTIC SODA SOLUTION

This is prepared by dissolving 45 grammes of caustic soda (about $2\frac{1}{4}$ sticks) in a litre of distilled water. It is standardised by titrating 25 c.c. against normal sulphuric acid, using methyl orange as indicator.

EVALUATION OF SULPHURIC ACID BY NORMAL CAUSTIC SODA SOLUTION

The strength of sulphuric acid can be ascertained fairly well from its density, but this is not reliable when it is very nearly pure. In this case about 0·5 gramme should be weighed out in a stoppered weighing bottle, and afterwards rinsed out into a beaker of water. The acid is then titrated with the soda solution, using methyl orange as indicator. The equation :—

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$$

shows that 49 grammes of acid reacts with 40 grammes of soda, *i.e.* with a litre of normal soda solution, so that each c.c. of soda solution corresponds to 0·049 gramme of sulphuric acid.

ESTIMATION OF LIME BY NORMAL ACID AND ALKALI

0·7 gramme of lime is dissolved in 30 c.c. of normal hydrochloric acid. Do not filter the solution. Methyl orange is then added and the excess of acid titrated with normal caustic soda solution. The difference gives the volume of acid used in neutralising the lime. In this method the lime present as calcium carbonate is also estimated.

PREPARATION OF DECINORMAL PERMANGANATE SOLUTION

This is prepared by dissolving 3·16 grammes of potassium permanganate and diluting the solution to 1 litre. It is standardised by titration against a solution of 0·980 gramme of ferrous ammonium sulphate in a little dilute sulphuric acid, which is equivalent to 25 c.c. of the decinormal solution : the permanganate is run in from the burette until the solution just acquires a faint permanent pink colour.

EVALUATION OF BOG IRON ORE BY PERMANGANATE SOLUTION

The sample is prepared by rubbing it through a stout 10-mesh sieve. It is then dried on a clock glass at 105° C. until no further loss in weight occurs. The loss in weight gives the moisture present. One gramme of

the dried material is burnt off at a dull red heat, the loss in weight giving the organic matter and combined water. The calcined residue is repeatedly digested with small quantities of strong hydrochloric acid until it is quite white, showing that all the iron has been extracted. A drop of the last lot of acid should give no red colour with potassium thiocyanate solution. The acid extract is diluted with $1\frac{1}{2}$ times its own volume of water and heated to boiling. Stannous chloride solution (29 grammes dissolved in 330 c.c. of concentrated hydrochloric acid and diluted to a litre) is then run in gradually till the yellow colour is just discharged and a drop gives no red colour with thiocyanate solution.

Cool and add 5 c.c. of saturated mercuric chloride solution, which should give a white (not grey) precipitate. No precipitate means that too little stannous chloride has been used: a grey precipitate shows that too much has been added. Add to the liquid 300 c.c. of distilled water and 25 c.c. of Reinhardt's solution (20 grammes manganese sulphate, 100 c.c. each of water, cold 40 per cent. sulphuric acid, and phosphoric acid). Titrate the solution as rapidly as possible with permanganate solution until a pink colour is obtained. It is better to put a little of the solution aside: after rapidly adding the permanganate to the rest till it is pink, rinse this in and proceed more carefully. Each c.c. of $\frac{N}{10}$ permanganate solution corresponds to 0·007984 gramme of ferric oxide Fe_2O_3.

ESTIMATION OF MANGANESE DIOXIDE IN WELDON MUD

The moisture is removed and estimated in the usual way. 0·2 gramme of the dry mud is weighed out, and dissolved by boiling in a conical flask with 20 c.c. of dilute sulphuric acid and 50 c.c. of approximately $\frac{N}{10}$ oxalic acid solution, containing 63 grammes per litre. The solution is diluted with 200 c.c. of hot water and titrated with permanganate solution.

In a similar manner 50 c.c. of the oxalic acid, acidified in the same manner, but without the mud, are titrated (hot) with permanganate solution. The difference gives the amount of permanganate equivalent to the manganese dioxide in the mud: 1 c.c. of $\frac{N}{10}$ permanganate $= 0{\cdot}00142$ grammes MnO_2.

DECINORMAL IODINE SOLUTION

This contains 12·65 grammes of iodine, which is first dissolved in 250 c.c. of water by the addition of about 18 grammes of potassium iodide, and then diluted to a litre. It is standardised against sodium thiosulphate solution containing 24·8 grammes per litre. Starch solution, freshly prepared by boiling a *little* soluble starch with about half a test-tube full of water, so as to obtain a clear solution, is employed as indicator; it is used cold. If the thiosulphate is in the burette, it is run into a measured volume (say 25 c.c.) of iodine solution till the colour of the latter almost disappears. Starch solution is then added, and gives a bright blue colour; more thiosulphate is then run in until this is discharged. The titration may be made equally well by running the iodine into the thiosulphate + starch until a permanent blue colour is obtained.

Several examples of the use of these solutions will be found in the chapter on AMMONIA LIQUOR.

EXAMINATION OF SPENT OXIDE

The moisture is determined by drying 5 grammes at 100° C. for three hours. The dry residue is extracted for two hours with freshly-distilled carbon disulphide in a Soxhlet apparatus. The solvent is then distilled off, using a tared flask, and the flask blown out with air and dried for two hours at 100° C., after which the sulphur is just fused by careful heating on a sand-bath. When cold, the flask is again blown out with air and weighed; the increase in weight gives sulphur + tar. 15 c.c. of concentrated sulphuric acid are then added, and the flask heated for two

hours at 100° C. After cooling the acid is diluted and the sulphur, etc., filtered off, washed and dried. The filter paper with the sulphur, etc., is then re-extracted with carbon disulphide, and the extract, which is pure sulphur, weighed as before. (*See Gas World*, 1920, **LXXII,** 320.)

50 grammes of moist spent oxide are extracted with water by rubbing in a mortar and allowing to stand for some hours. The aqueous extract may be examined for ammonia, ferrocyanides and thiocyanates by the methods described under ammoniacal liquor. The insoluble residue still contains ammonia and ferrocyanides (*e.g.* prussian blue). The latter may be extracted by trituration with 40 per cent. caustic soda solution. The alkaline solution is boiled with excess of ammonium chloride till ammonia ceases to be evolved, and any alumina precipitated is filtered off. The liquid is then slightly acidified and ferric alum solution added, the ferrocyanides being precipitated as prussian blue. This is filtered off, ignited and weighed as ferric oxide (1 gramme=1·54 grammes prussian blue).

ABSORPTIVE POWER OF BOG IRON ORE

A quantity of the material is placed in one limb of a weighed U tube, which is re-weighed to ascertain the amount taken. The other limb is then filled with calcium chloride, the two being separated by a cotton-wool plug. The whole is re-weighed. A stream of dry sulphuretted hydrogen is then slowly passed through as long as any increase in weight occurs, and the tube is then swept out with dry air and re-weighed. The increase in weight gives the weight of sulphuretted hydrogen absorbed.

QUICKLIME IN LIME

The titration method does not distinguish between quick and slaked lime. The amount of quicklime in any sample may, however, readily be found by weighing out about 5 grammes in a basin, slaking it carefully with a small quantity of water, drying at 105° C. and re-weighing. The increase in weight gives the water taken up by the

quicklime: each gramme of water corresponds to 3·11 grammes of quicklime.

SULPHUR IN PYRITES

About ·25 gramme of the finely-divided pyrites is treated with aqua regia in a porcelain basin and evaporated to dryness on a water bath; this is repeated twice. The third residue is moistened with concentrated hydrochloric acid and again evaporated to expel nitric acid. The residue is taken up with water and the solution slightly acidified with hydrochloric acid. It is then filtered, and the filtrate diluted to 250 c.c. The sulphate present is then precipitated by the addition of barium chloride solution just as when determining sulphur in coal.

VALUATION OF SODIUM NITRATE

This may be effected by reduction to ammonia, which is then estimated by distillation, as is fully described in the next chapter. The distillation flask contains 50 grammes of granulated zinc, broken small and mixed with half its weight of clean iron filings, recently ignited in a covered crucible. One gramme of sodium nitrate is brushed into the flask, into which 100 c.c. of 5 per cent. caustic soda solution is run. The receiver is charged with 20 c.c. of N acid. The flask is heated over a small flame (not to boiling) for an hour; the heat is then increased and the liquid slowly distilled.

The ammonia is absorbed by the acid, the excess of which is afterwards titrated with N alkali. Each c.c. of acid neutralised by ammonia represents 0·085 gramme of sodium nitrate.

Lunge's nitrometer may also be used for this determination.

CHAPTER III

AMMONIA LIQUOR AND AMMONIUM SULPHATE

AMMONIUM SULPHATE

(1) Ammonia (including Pyridine)

WEIGH out 1 gramme of the salt and transfer it to the flask of the ammonia distillation apparatus. Add about 150 c.c. of water, and connect with the condenser. In the receiver place 30 c.c. of normal sulphuric acid and one drop of methyl orange solution. The end of the condenser must be well covered. If during the distillation the red colour of the methyl orange is discharged more acid must at once be run in. Test the tightness of the connections by warming the air space in the distillation flask with a bunsen burner until several bubbles of air escape from the end of the condenser; withdraw the flame and note if the acid sucks back up the condenser tube.

Run in 30 c.c. of 10 per cent. caustic soda solution through the dropping funnel, and distil off the liberated ammonia. About one hour should suffice for this, not more than 50 c.c. being left in the flask. On lowering the beaker, the liquid dropping from the condenser should be without action on glazed red litmus paper. Sucking back may be checked by opening the tap of the dropping funnel for a moment, first taking care that the end of the stem is covered with liquid.

Rinse the condenser into the beaker and titrate the excess of acid with normal caustic soda solution. Difference gives the acid neutralised by ammonia (each c.c. = 0·017 gramme of NH_3).

(2) Dirt and Free Acid (Sulphuric)

Weigh out 50 grammes of the salt and dissolve in hot water. Filter off the dirt through a weighed Gooch crucible packed with paper-pulp, wash it well, dry in the steam oven and weigh. A brown sticky residue is tar; blue is prussian blue; bright yellow probably arsenic sulphide.

To the filtrate add one drop of methyl orange, and titrate the free acid with $\frac{N}{10}$ caustic soda solution (1 c.c. = 0·0049 gramme H_2SO_4).

(3) Moisture

This is estimated by drying a known weight at 105° C.

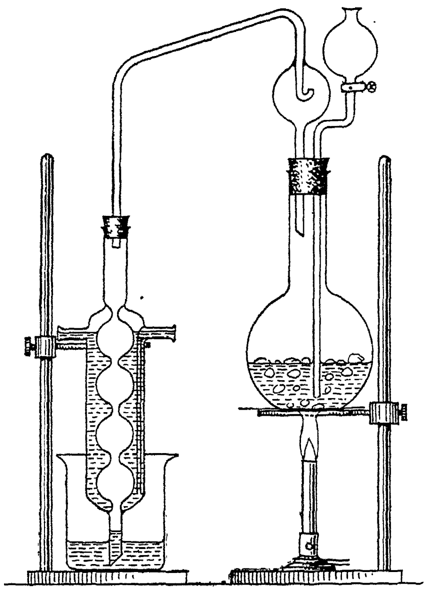

FIG. 4.—AMMONIA DISTILLATION APPARATUS.

till no further loss in weight occurs, just as in the case of coal.

(4) Pyridine

The solution from the free acid determination may be used. It is made up to 500 c.c. and 250 c.c. taken; 5 c.c. of $\frac{N}{10}$ caustic soda solution are added, and it is distilled in a

litre flask. The vapours pass through a second flask containing sodium hypobromite solution,[1] which oxidises the ammonia to nitrogen, and thence to a condenser and receiver containing 10 c.c. of $\frac{N}{10}$ acid. The excess of acid is titrated with $\frac{N}{10}$ alkali, using methyl orange (or better congo red) as indicator (1 c.c. $= 0{\cdot}0079$ gramme C_5H_5N).

(5) Thiocyanates, etc.

Generally speaking these will be absent from ammonium sulphate crystallised from acid solution as usual. If, however, the crystallisation is from ammoniacal solution, pyridine will be absent and thiocyanates present. They may be estimated, after filtering off the dirt, using the method given under Ammonia Liquor.

AMMONIA LIQUOR

(*See* the Alkali Inspectors' Annual Reports, especially No. 40.)

(1) "Free" Ammonia (including Pyridine)

(*a*) 25 c.c. of liquor are diluted to 250 c.c. (more or less according to the colour), a drop of methyl orange is added, and the ammonia titrated with normal acid.

(*b*) 25 c.c. of liquor are diluted to 300 c.c., and distilled (without alkali) in the ammonia distillation apparatus until reduced to 150 c.c. The ammonia is collected in 30 c.c. of normal acid (or a few c.c. more than used in the direct titration), and the excess titrated by normal soda (1 c.c. $= 0{\cdot}017$ gramme NH_3). "Free" ammonia includes the carbonate, sulphide, cyanide and acetate.

(2) "Fixed" Ammonia

To the 150 c.c. left from the free ammonia distillation add 30 c.c. of 10 per cent. caustic soda, and distil off the ammonia as before till the volume is reduced to 30–40 c.c. "Fixed" ammonia includes the chloride, sulphite, sulphate, thiocyanate, thiosulphate, thiocarbonate and ferrocyanide.

[1] Add 1 c.c. bromine to 25 c.c. 10% NaOH.

(3) Total Ammonia

Dilute 25 c.c. of liquor to 150 c.c., and add 30 c.c. of 10 per cent. caustic soda, and distil off the ammonia as usual. Verify that free ammonia + fixed ammonia = total ammonia.

(4) Pyridine

250 c.c. of liquor are neutralised with normal acid (the volume being calculated from the free ammonia titration); 5 c.c. of $\frac{N}{10}$ caustic soda solution are then added (verify the alkalinity of the solution with red litmus paper) and the pyridine distilled off and estimated as described under ammonium sulphate (1 c.c. = 0·0079 gramme C_5H_5N).

(5) Carbonate

Dilute 10 c.c. of liquor to 400 c.c.; add 10 c.c. of ammoniacal calcium chloride[1] (1 c.c. = 0·044 gramme CO_2), and heat the whole in a stoppered bottle for $1\frac{1}{2}$ to 2 hours in a water-bath at 100° C. Cool a little, decant through a filter and wash the precipitate by decantation. Dissolve it in 25 to 50 c.c. of $\frac{N}{2}$ HCl. Add to the solution the incinerated filter-paper. Titrate the excess of acid with $\frac{N}{2}$ alkali (1 c.c. = 0·0155 gramme H_2CO_3).

(6) Chloride

250 c.c. of liquor are boiled (to expel sulphides, etc.) and made up to 250 c.c.; 10 c.c. of boiled liquor are diluted to 150 c.c. and 20 c.c. of hydrogen peroxide (10 vol.) added, and the solution boiled till nearly decolorised. Add 10 to 15 drops of potassium chromate solution and boil five minutes longer. Filter if necessary, neutralise with a little sodium bicarbonate, and titrate with $\frac{N}{10}$ silver nitrate solution as described in the chapter on WATER ANALYSIS 1 c.c. = 0·00365 gramme HCl).

[1] 111 grammes $CaCl_2$ and 140 c.c. conc. ammonia per litre.

(7) Sulphate

250 c.c. of liquor are boiled down to 10 c.c., 2 c.c. of concentrated hydrochloric acid added and the evaporation continued to dryness. Take up the residue with water, filter, and make up the filtrate to 250 c.c. Precipitate the sulphur in 100 c.c. of this solution by barium chloride solution, and collect and weigh the barium sulphate (1 gramme = 0·4202 gramme H_2SO_4 = 0·1374 gramme S).

(8) Thiocyanate

Take 50 c.c. of the boiled liquor (*see* "Chloride" above) and remove any ferrocyanide present by precipitation with ferric alum solution as prussian blue; usually this will not be necessary. Saturate the cold solution with sulphur dioxide, add excess of copper sulphate solution, and allow to stand for one to two hours in a corked flask. Filter cold, wash the precipitate well with hot water, to which sodium sulphate may be added if the precipitate tends to pass through the paper. The final washings must give no black colour with ammonium sulphide. Wash the precipitate (which should be white) back into the flask, washing the paper with dilute nitric acid. Add 1 to 2 c.c. of concentrated nitric acid and boil until a green solution is obtained; if discoloured by organic matter evaporate and ignite and take up with nitric acid. Cool and neutralise with solid sodium carbonate, acidify with acetic acid, add potassium iodide, and titrate the iodine liberated with $\frac{N}{10}$ thiosulphate solution (1 c.c. = 0·0059 gramme HSCN = 0·0032 gramme S).

(9) Sulphide

The total iodine value of the liquor is found by a preliminary titration of 10 c.c. of liquor (diluted to 500 c.c., and acidified with hydrochloric acid), with $\frac{N}{10}$ iodine solution. The amount of liquor to be taken for the experiment should correspond to about 25 c.c. of $\frac{N}{10}$ iodine solution. The

volume so calculated is added to excess of ammoniacal zinc chloride solution diluted to 80 c.c. with warm water. The precipitated zinc sulphide is well washed with warm water, and then washed into 25 c.c. of $\frac{N}{10}$ iodine solution acidified with hydrochloric acid. The filter paper is washed with cold dilute hydrochloric acid. Stir vigorously until all the sulphide is dissolved, dilute, and titrate the excess of iodine with $\frac{N}{10}$ thiosulphate solution (1 c.c. = 0·0017 gramme H_2S = 0·0016 gramme S).

(10) Sulphite and Thiosulphate

This method is only approximate. The sum of the two constituents is given by the difference between the total iodine value of the liquor and that due to the sulphide.

To 10 c.c. of liquor is added 10 c.c. of ammonium polysulphide solution (made by saturating ammonium sulphide with sulphur and diluting 1 in 50). Let this stand for twenty minutes, and remove sulphides by precipitation with ammoniacal zinc chloride solution: filter and wash the precipitate. Titrate the filtrate with $\frac{N}{10}$ iodine solution. The use of polysulphide converts sulphites into thiosulphates with a 50 per cent. reduction of iodine value: accordingly twice the difference between the two iodine values (the first representing sulphite + thiosulphate, and the second $\frac{1}{2}$ sulphite + thiosulphate) represents the sulphite. c.c. $\frac{N}{10}$ iodine solution = 0·0114 gramme $H_2S_2O_3$ (containing 0·0064 gramme S) = 0·0041 gramme H_2SO_3 (containing 0·0016 gramme S).

(11) Polysulphides

These can only be met with in absence of cyanides and sulphites, which is very rare. They may be estimated by adding excess of $\frac{N}{10}$ sodium sulphite solution (standardised

against iodine), removing sulphides as in (9) and titrating the filtrate against iodine. Subtract this from the calculated iodine value of the sulphite solution + liquor—sulphides. The loss of iodine value gives the iodine equivalent of the polysulphides (1 c.c. $\frac{N}{10}$ iodine solution = 0·0066 gramme H_2S_2 = 0·0064 gramme S).

(12) Total Sulphur

50 to 100 c.c. of liquor is delivered drop by drop into a flask containing excess of bromine, covered with dilute hydrochloric acid. The solution obtained is evaporated to dryness and the residue taken up with boiling water, filtered (a yellow precipitate = tribromphenol) and made up to 250 c.c. 100 c.c. is then precipitated with barium chloride solution, and the barium sulphate weighed (1 gramme = 0·1374 gramme S).

(13) Ferrocyanide

The prussian blue precipitate obtained under (8) may be ignited and weighed as Fe_2O_3 (1 gramme = 2·70 grammes $H_4Fe(CN)_6$).

(14) Cyanide

50 c.c. of liquor are taken and diluted to 250 c.c., 25 c.c. of 20 per cent. lead nitrate solution is added, and the hydrocyanic acid distilled off (in an ammonia-distillation apparatus) and collected in 10 c.c. of 10 per cent. caustic soda solution. This solution is then titrated either with $\frac{N}{10}$ silver nitrate solution, with the addition of a crystal of potassium iodide (till a faint permanent turbidity occurs) or, after neutralising and then adding a little sodium bicarbonate, with $\frac{N}{10}$ iodine solution (starch indicator).

1 c.c. = 0·0054 gramme HCN — $AgNO_3$ solution.

1 c.c. = 0·00135 gramme HCN — KI_3 solution.

For phenols, *see* Skirrow, *J.S.C.I.* 1910, **29**, 319.

CHAPTER IV

BENZOL

ALLEN'S TEST

THE rapid valuation of crude benzol is effected by measuring 100 c.c. in a measuring cylinder and transferring it as completely as possible to an 8-oz. retort, the moist cylinder being then used as a receiver. The retort is connected to a water condenser, previously rinsed with crude benzol and allowed to drain. The temperature of the liquid is indicated by a "benzol thermometer" (reading from 70° C. to 130° C. in fifths of a degree) placed with the lower end of the bulb $\frac{3}{8}$ of an inch from the bottom (inner surface) of the retort. This must be adjusted with the retort empty as it is almost impossible to judge the distance with the benzol in the retort, owing to refraction.

The benzol is distilled over a small bare flame, the size of a hazel nut, screened by a cylinder of wire gauze, at the rate of two drops per second. The temperature at which the first drop distils is noted, and also the volume of the distillate at 85° C. (if any), 100° C. and 120° C. At 120° C. the distillation is stopped and, after cooling, the contents of the retort are drained into the receiver. The deficiency from 100 c.c. gives the loss on distillation, which should not exceed 2 c.c. Frequently the distillation is continued to 170° C. (after stopping at 120° C.) to estimate roughly the solvent naphtha.

The percentage distillate up to 120° C., plus the loss on distillation, gives the quality of the benzol. Thus a benzol giving 65 c.c. would be described as 65's benzol and would contain perhaps 45 per cent. of pure benzene.

The density of the benzol at 15° C. should also be taken, with a hydrometer.

ANALYSIS OF CRUDE BENZOL

250 c.c. of the sample are distilled from a round-bottomed flask fitted with a 12-bulb pear column (or other efficient column) at the rate of about 4 c.c. per minute, and the distillate up to 170° C. collected and measured. The residue is also cooled and measured, and the loss on distillation noted. The residue is calculated as a percentage of the original 250 c.c.

The distillate is shaken with 8 per cent. of concentrated sulphuric acid for five minutes, allowed to settle for fifteen minutes, and the separated oil washed successively with water, 20 c.c. of aqueous caustic soda (10 per cent.) and finally with 20 c.c. of water. If an emulsion is formed during the washing, the separating funnel should be warmed by blowing steam on it, when a separation can usually be secured.

The volume of washed oil is measured, and the loss due to washing noted, and calculated as a percentage on the original volume of crude benzol. The washed oil is dried for thirty minutes with calcium chloride and filtered through a little cotton-wool, placed in the stalk of a funnel, into a round-bottomed flask, the drying material and filter being washed with 2–3 c.c. of pure xylene.

The dried oil thus obtained is then distilled with a Young 12-bulb pear column or rod-and-disc column at the rate of about 4 c.c. per minute, and the following distillates collected and measured :—

(1) Fraction up to 90° C.

(2) Fraction 90° C.–140° C.

If the thermometer does not reach 140° more xylene is added to the residue in the flask, and the distillation then continued to 140° C. This xylene must *not* be added until the "fraction up to 90° C." has been distilled off. The residue above 140° C. is also cooled, and measured, to give the loss on distillation.

Fraction (1) is a mixture of benzene and toluene, and is examined by Spielmann's test.

Fraction (2) is a mixture of benzene, toluene and xylene. 40 c.c. (or the whole, if less) is mixed with 50 c.c. of pure toluene and made up to 100 c.c. with pure benzene. The mixture is then examined by Colman's test, or if desired Northall-Laurie's test may be used.

The residue contains xylenes and higher homologues, and together with the xylene in fraction (2), is classed as "solvent naphtha." The total solvent naphtha is found by difference.

The total benzene and toluene is found by addition of the amounts found in the first two fractions, subtracting, of course, that added to fraction (2).

We have found, contrary to expectation, that the method gives good results in inexperienced hands: the maximum error in determining each constituent is about 1 per cent. of the whole.

SPIELMANN'S TEST

100 c.c. of the mixture (of benzene and toluene) is distilled in a standard 100 c.c. Engler distillation flask at the rate of 7 c.c. per minute, until the temperature (registered by a "benzol thermometer" placed with the top of its bulb opposite the side tube) reaches 85° C., corrected. Actually the burner is extinguished at about 84·8° C.: the temperature continues to rise for a little after removing the flame. The condenser is allowed to drain, and the percentage distillate is read off. By reference to a graph (easily constructed by the use of known mixtures)[1] the percentages of benzene and toluene are found. The thermometer correction is found by taking the boiling point of water at the time of the experiment with the thermometer used, in a similar Engler flask. If this is 99·6° C. the distillation would be stopped at 84·6° C.; if 100·2° C., at 85·2° C.; and so on. If necessary less than 100 c.c. may be used for the test, with some loss of accuracy.

[1] *See* Appendix.

COLMAN'S TEST (**for Benzene and Toluene in commercial washed Toluene**)

100 c.c. of the sample is distilled exactly as above; the distillation being interrupted at (*a*) 104·7° C., (*b*) 115·9° C. (both corrected). From the volumes distilling below 104·7° C. and above 115·9° C. respectively, the percentages of benzene and toluene are ascertained by reference to a chart prepared by Colman by the use of known mixtures.[1] The apparatus is rinsed out with toluene and allowed to drain before distilling. The sample is measured in a 100 c.c. cylinder, drained into the distillation flask, and the moist cylinder used as receiver. The loss on distillation should not exceed 0·5 c.c. An approximate correction for paraffins may be made by taking the density, at 15·5° C., of the fraction below 104·7° C., and of the fraction between 104·7° C. and 115·9° C. For each 0·001 that the first fraction is below 0·873, subtract 1 per cent. of the amount of benzene found, and for each 0·001 that the middle fraction is below 0·870, subtract $\frac{2}{3}$ per cent. of the amount of toluene found, the deductions being calculated as "paraffins."

NORTHALL-LAURIE'S TEST (**for Benzene and Toluene in commercial washed Toluene**)

200 c.c. of the sample are placed in a distilling flask of just sufficient capacity, with the neck cut off close above the side tube. The contents are distilled at the rate of 7 c.c. per minute through an efficient condenser, into a 50 c.c. measuring cylinder. When 50 c.c. have distilled the receiver is quickly changed for 100 c.c. cylinder. When a further 98·5 c.c. have distilled the flame is extinguished; on allowing the condenser to drain, 100 c.c. will collect. If milky, the first fraction is dried by shaking with a fragment of calcium chloride. The boiling points of the first and last 50 c.c. are determined in a special apparatus, and the percentages of benzene and toluene found by reference to a chart constructed, using known mixtures.[1]

[1] *See* Appendix.

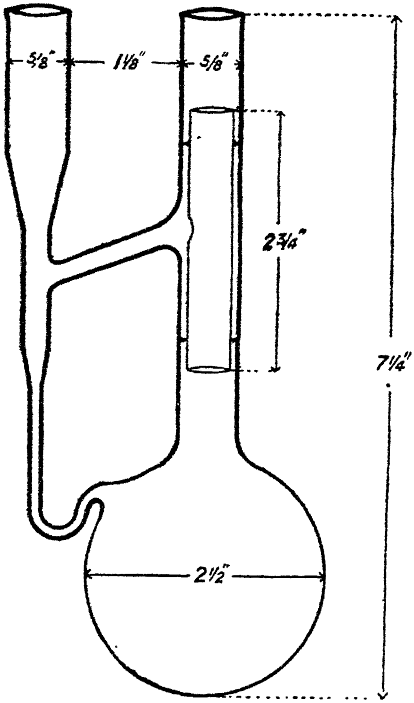

FIG. 5.—BOILING-POINT APPARATUS FOR NORTHALL-LAURIE TEST.

The boiling point apparatus (FIG. 5) is attached to a reflux condenser and boiled at such a rate that the condensed liquid runs back at the uniform rate of one drop per second. After ten minutes the temperature should be constant and is read. It must be corrected—

(1) for barometric pressure, by means of *Table* 1;

(2) for exposed stem, by the reading of an auxiliary thermometer placed with its bulb half-way up the exposed thread, and *Table* 2.

TABLE 1.—CORRECTIONS FOR BAROMETRIC PRESSURE

Pressure.		Correction.		Pressure.		Correction.	
770	753	− ·45	+ ·3	761	744	− ·05	+ ·75
769	752	− ·4	+ ·35	760	743	+ ·0	+ ·8
768	751	− ·35	+ ·4	759	742	+ ·05	+ ·85
767	750	− ·3	+ ·45	758	741	+ ·1	+ ·9
766	749	− ·25	+ ·5	757	740	+ ·15	+ ·9
765	748	− ·2	+ ·55	756	739	+ ·2	+ ·95
764	747	− ·2	+ ·6	755	738	+ ·2	+ 1·0
763	746	− ·15	+ ·65	754	—	+ ·25	—
762	745	− ·1	+ ·7				

TABLE 2.—TEMPERATURE CORRECTIONS TO BE ADDED

Length of Exposed Mercury Thread.	Difference of Thermometer Readings.						
Degrees	50°.	60°.	70°.	80°.	90°.	100°.	110°.
10	·07	·09	·10	·12	·13	·14	·16
20	·15	·17	·20	·23	·26	·29	·32
30	·22	·26	·30	·34	·39	·43	·48
40	·29	·35	·40	·46	·52	·57	·63
50	·36	·43	·50	·57	·65	·71	·79
60	·43	·52	·60	·68	·78	·86	·95
70	·50	·60	·70	·80	·91	1·00	1·10
80	·57	·69	·80	·91	1·03	1·14	1·27
90	·65	·77	·90	1·02	1·17	1·29	1·42
100	·72	·86	1·00	1·14	1·30	1·43	1·57

CARBON DISULPHIDE

100 c.c. of benzol are well shaken in a separating funnel with an equal volume of alcoholic potash solution, used in three or four portions. The potash solution is made by dissolving 10 grammes of potash in a little water and making up to 100 c.c. with alcohol.

The separated alkaline solution is then oxidised by adding a few drops of bromine and boiling under reflux for an hour. It is then neutralised with 20 c.c. of concentrated hydrochloric acid, and after boiling off the alcohol, the sulphate formed is precipitated with barium chloride solution.

1 gramme $BaSO_4 = 0.163$ gramme CS_2.

THIOPHENE

In this method the thiophene is precipitated in combination with basic mercuric sulphate by the use of Denige's reagent, which is best prepared as follows :—

70 grammes of mercuric sulphate are taken and 190 c.c. of 93 per cent. sulphuric acid added, and then (*after* the

acid) a litre of water. The mixture is heated till all is dissolved.

2 c.c. of the benzol are mixed with 30 c.c. of methyl alcohol (free from acetone) and 10 c.c. of Denige's solution is then added quickly, with stirring. A precipitate of the composition $SO_4(HgO)_2 : Hg : C_4H_4S$ separates. After twenty minutes the precipitate is filtered off (using a tared filter-paper or a Gooch crucible, packed with paper pulp and dried at 105° C.), washed with hot water until 25 c.c. of the washings give a distinct alkaline reaction on adding phenol-phthalein solution and one drop (0·05 c.c.) of $\frac{N}{2}$ caustic soda solution, dried at 105° C., and weighed. 0·1034 times the weight of the precipitate gives the weight of thiophene in the 2 c.c. of benzol. A blank experiment should be made using 2 c.c. of pure benzene.

If thiophene is in excess the composition of the precipitate is different, *viz.*, $SO_4(HgOH)_2SO_4C_4H_4S$. Hence the need of adding the precipitant quickly. The filtrate may be kept for recovery of methyl alcohol and benzene free from thiophene.

TOTAL SULPHUR

This test consists in burning the benzol (or other light oil) in air in presence of a catalyst, and absorbing the sulphur dioxide formed.

The combustion tube consists of moderately hard glass, about 30 cm. long and 13 mm. in diameter, packed with platinised asbestos. One end is drawn out and connected to a filter-pump through an absorption bulb, containing saturated caustic potash solution or alkaline hypobromite solution. The other end, which is away from the heated (asbestos) portion, has a rubber cork and a T-piece. The lower branch[1] of this is connected with a stoppered U-tube, packed with cotton-wool, standing in a water-bath; the upper branch is connected with a flask of water through which the air bubbles by an inlet tube dipping into the water,

[1] In the figure the upper branch is shown connected to the U-tube; the other way is, however, preferable.

the supply being adjusted by the length of tube immersed.
2 c.c. of benzol are introduced into the limb of the

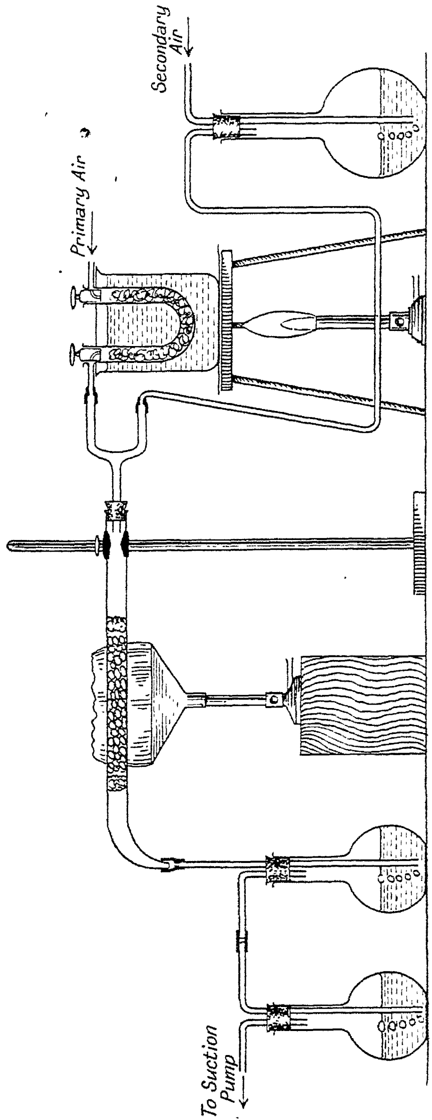

FIG. 6.—ESTIMATION OF TOTAL SULPHUR IN BENZOL.

U-tube adjacent to the combustion tube and the U-tube is immediately restoppered to prevent evaporation. The

platinised asbestos is heated moderately by a spread-out bunsen flame and a current of air drawn through the apparatus. The stopper of the U-tube is partly turned so as to draw a little air through the benzol. Combustion takes place and a glow is observed in the combustion tube. When the glow ceases the tap of the U-tube is opened full and the last traces of benzene expelled by warming the U-tube in hot water.

When the combustion is finished the contents of the absorption bulb are washed into a beaker, 10 c.c. of saturated bromine water are added and then strong hydrochloric acid till acid. The liquid is then diluted, boiled, and 10 c.c. of 10 per cent. barium chloride solution added, drop by drop. The precipitated barium sulphate, after standing overnight, is collected and weighed exactly as in estimating sulphur in coal.

NATIONAL BENZOLE ASSOCIATION SPECIFICATION

The National Benzole Association's specification for Benzol for use as motor spirit is as follows :—

(1) *Specific Gravity :* ·870 to ·885.

(2) *Distillation test* (by flask) : Benzol should give a distillate of not less than 75 per cent. to 80 per cent. at 100° C.

(3) *Sulphur :* the total sulphur shall not exceed 0·40 per cent.

(4) The Benzol shall be entirely free from water.

(5) *Colour :* Water white.

(6) *Rectification test :* 90 c.c. of the sample shaken with 10 c.c. of 90 per cent. sulphuric acid shall not give more than a light brown colour to the acid layer.

(7) Benzol shall be entirely free from acids, alkalies and sulphuretted hydrogen.

(8) Benzol shall not freeze at 25° F. below the freezing point of water.

DENSITY OF BENZENE

The effect of toluene, xylene, petrol or carbon disulphide on the density of benzene may be calculated by the mixture

rule. Each gramme of naphthalene present in 100 c.c. increases the density by ·0013. *Cf.* the following tables, made by students in our laboratory.

BENZENE + TOLUENE

Benzene Per cent.	Toluene Per cent.	S.G. Calculated.	S.G. Observed.
100	0	(·880)	·880
90	10	·879	·879
80	20	·878	·878
70	30	·877	·877
60	40	·876	·876
50	50	·875	·875
40	60	·874	·874
30	70	·873	·873
20	80	·872	·872
10	90	·871	·871
0	100	(·870)	·870

BENZENE + NAPHTHALENE

Grammes $C_{10}H_8$ per 100 c.c.	S.G. Observed.
0	·880
1	·882
3·33	·885
6·67	·889
10	·893
13·33	·897
20	·9055
26·67	·912

BENZENE + CARBON DISULPHIDE.

Benzene Per cent.	CS_2 Per cent.	S.G. Calculated.	S.G. Observed.
100	0	(·880)	·880
98	2	·888	·888
96·1	3·9	·895	·895
94·2	5·8	·903	·902
92·5	7·5	·910	·909
90·7	9·3	·9165	·916
0	100	(1·275)	1·275

BENZENE + PETROLEUM ETHER

Benzene Per cent.	Petrol Per cent.	S.G. Calculated.	S.G. Observed
100	0	(·880)	·880
98	2	·876	·877
96·1	3·9	·872	·873
94·2	5·8	·8685	·869
92·5	7·5	·865	·866
90·7	9·3	·862	·862
0	100	(·6815)	·6815

NAPHTHALENE IN WASHED CRUDE BENZOL

This may be roughly found by taking the density of the benzol and then distilling it up to 120° C., using a fractionating column, and taking the density of the distillate. Multiply the difference in density by 700 and the result is the approximate weight of naphthalene in 100 c.c. Crude benzol may be tested by this method after washing.

CHAPTER V

FUEL OILS

DENSITY

ALL determinations of fuel oils must be made at a definite temperature; for comparative purposes 15° C. should be adopted.

The quickest method is by the use of a hydrometer. In using the instrument take care that it is floating freely, and that the stem is moistened a little beyond the highest part immersed. The correct reading is the point on the scale in the plane of the liquid surface, not the point reached by the liquid immediately adjacent to the stem. A hydrometer is easily standardised by the use of liquids of known density, determined by one of the following methods.

Westphal's hydrostatic balance is a rapid and fairly accurate method. One arm consists of a heavy bob, the other is divided into tenths, and carries a glass plummet which dips into the liquid under test. The balance is brought into equilibrium by addition of a series of riders to the graduated beam, each rider being $\frac{1}{10}$ of the weight of the next heavier. Reading the position of the riders on the beam in order of magnitude gives the successive decimal places in the density.

The specific gravity bottle is a small flask with a perforated stopper. It is weighed dry. It is then filled to the brim with the liquid under examination and immersed in a water bath at any desired temperature. When it has assumed this temperature the stopper is dropped in and allowed to sink into position under its own weight; by this means inclusion of air bubbles is avoided. The outside is

quickly wiped dry (care being taken not to heat the contents). The top of the stopper is wiped with a finger tip, leaving the perforation full of liquid. The bottle is then weighed.

The exact capacity of the bottle is got by weighing it full of distilled water at a definite temperature (15° C.). By reference to a table of the apparent density of water (weighed in air in glass vessels with brass weights) the capacity is readily found.

By dividing the weight of oil by the volume the density is found; for accurate work an allowance for the buoyancy of air must be made, by adding to the observed weight of the oil that of an equal volume of air, minus the volume occupied by the brass weights (density 8·0). The density of air may be taken as 1·2 grammes per litre. Tables are available to facilitate the calculation.

FLASH POINT

This may be determined in the Abel-Pensky apparatus (FIG. 7). The oil is contained in a closed metal vessel surrounded by a water jacket at 130° F.: it should initially be at about 60° F. When it reaches 66° F. testing is begun, and is carried out at each successive degree rise of tempera-

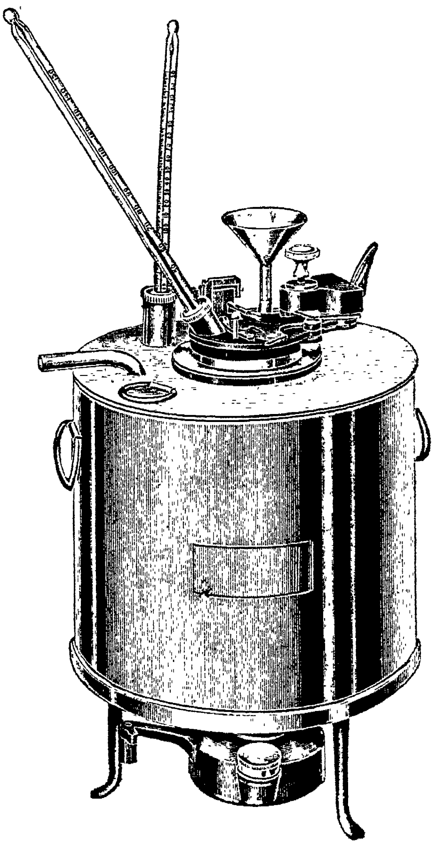

FIG. 7.—ABEL-PENSKY FLASH-POINT APPARATUS.

ture. The test consists in the application of a small flame (a gas flame, or colza oil flame in a little pivoted lamp) to the vapour space inside the vessel. This is done by a clockwork device which opens a slide and tilts the flame inside on touching a spring. The temperature at which the vapour first ignites is the flash point.

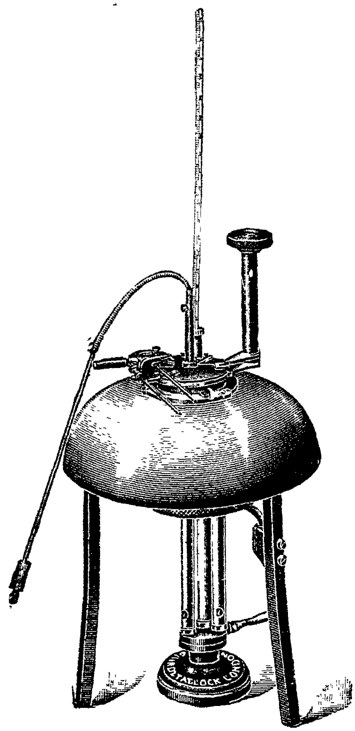

FIG. 8.—PENSKY-MARTIN FLASH-POINT APPARATUS.

For heavy oils the Pensky-Martin apparatus (FIG. 8) is used, in which the water jacket is replaced by a massive iron container, which is heated over a Bunsen burner.

The flash point may be corrected for barometric variations by adding 1·6° F. for every inch below 30 in., and *vice versa*.

In default of other apparatus the "open" test may be used. In this the oil is heated in an open crucible, with a thermometer dipping into it. A lighted taper is passed just above the surface at intervals, and when the flame momentarily covers the whole surface the flash point is reached. The test may be continued until the burning persists, this temperature being known as the "fire test." "Open" flash points are about 27° F. higher than "closed" flash points.

VISCOSITY

This is simply a comparative test, the oil being allowed to flow from a given orifice into a measuring flask until a definite volume has collected. Usually rape oil, density

·9142, is used as standard, the viscosity being taken as 100. Redwood's viscometer (FIG. 9) is generally employed.

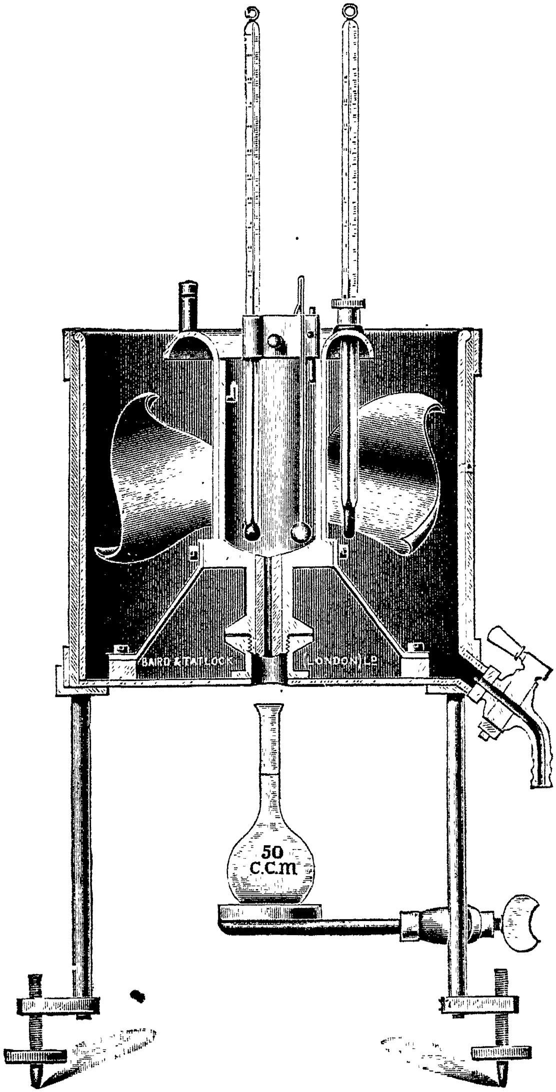

FIG. 9.—REDWOOD VISCOMETER.

The oil is brought to the desired temperature and kept at it for some time. Meanwhile the jacket of the instru-

ment is adjusted to the same temperature. The oil is then poured into the vessel up to a definite mark. On lifting a ball-valve the oil flows into a measuring flask, and the time taken for 50 c.c. to collect is noted. The density is also taken. A corresponding test with rape oil may be made; as, however, samples differ among themselves, the time of flow may be taken as 535 seconds.

The viscosity is given by the formula $100 \times \frac{\text{time}}{535} \times \frac{\text{density}}{\cdot 9142}$.

DISTILLATION

This is carried out in a standard 100 c.c. Engler distillation flask. It is usual to measure the distillate every 25° C., beginning at 75° C., 100° C., 125° C., etc.

The fraction below 150° C. may be described as naphtha, and the fraction 150° C.–300° C. as burning oil or kerosene. A "straight" distillation may be made, but a closer approximation to the results on the large scale may be obtained by Engler's method of allowing the temperature to fall 20° C. at each change-over point, and distilling up to the temperature again, the process being repeated until no further distillate can be obtained at that temperature. This is very tedious and a very similar result can be quickly obtained by the use of a round flask and a four-bulb Young pear-shaped column.

SULPHUR

For naphtha the method described under Benzol may be used. For heavier oils the best method is combustion in the bomb calorimeter (*see* page 114). The Referees' apparatus for sulphur in gas may also be used, the burner being replaced by a small oil lamp, weighed before and after the experiment.

BENZENES, NAPHTHENES AND PARAFFINS

The oil is washed as described under benzol to remove unsaturated hydrocarbons, etc. The oil is next treated

with fuming sulphuric acid as long as any diminution in volume takes place, the loss giving the benzene hydrocarbons. The residue, consisting of paraffins and naphthenes, is treated with fuming nitric acid. This oxidises the naphthenes to benzenes, which are then nitrated. The residue, after washing, consists of paraffins somewhat contaminated with nitro-compounds, which may be removed by distillation.

The operations can be greatly hastened by applying heat. For this purpose a vessel with a ground-in condenser is required, and great care is necessary to avoid loss. The density of the oil should be taken at each stage.

CHAPTER VI

COAL TAR

THE distillation of coal tar is carried out in the small copper still (Fig. 10), which is provided with a "top

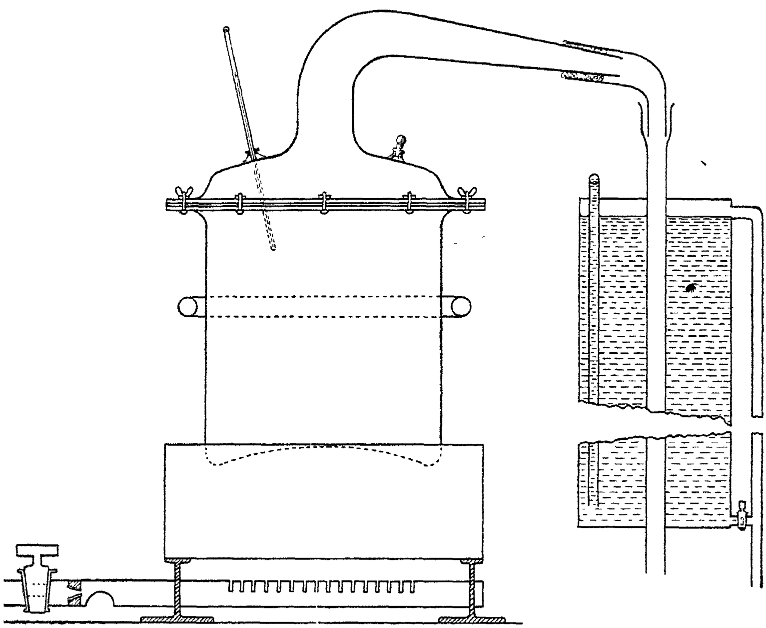

Fig. 10.—Laboratory Tar Still.

heat" in the form of a semicircle of small gas jets embracing the still about two-thirds up, a "bottom heat," a tap for running off pitch, a thermometer, and a dead-weight safety valve.

Any water that separates from the tar before distillation

is poured off, measured, and preserved in a corked flask. The density of the tar is taken. Six litres of tar are then charged into the still and the swan-neck, which must be cleaned as much as possible, is connected by a flange joint to the still, and by a glass adapter to the vertical condenser. The joints are packed with asbestos.

The distillation is started using the top heat only, and carried on by this means as long as anything will distil. In this manner the water and light oil (up to 170° C.) can be expelled without fear of priming. This distillate is separated, the volumes of ammoniacal liquor and of light oil being measured.[1] The density of the oil is also taken by a hydrometer (or Westphal balance). The ammonia in the liquor is estimated as usual (for total ammonia). The following fractions are then collected :—

170°–230° C. (Middle oil).
230°–270° C. (Creosote oil).
270°–360° C. (Anthracene oil).

As soon as the bottom heat is brought into use the top heat is turned out, and the flow of water through the condenser stopped. At about 200° C. the water is run out of the condenser. The latter is carefully watched and if it shows signs of blocking up with naphthalene, etc., hot water is poured into it.

The volumes and densities of the heavier fractions must be taken while they are hot and free from solid matter, the two determinations being carried out at the same temperature, and the weights of the oils deduced. Finally the pitch is allowed to cool, and is then run into a tared tin vessel, and, when cold, weighed. All fractions are calculated as percentages of the tar.

Owing to the superheating action of the top heat on the vapour, the thermometer readings in the early part of the distillation will be too high. The presence of the water also gives a steam-distillation effect, whereby higher boiling

[1] If the oil and water do not separate readily, add a measured volume of pure benzene.

oils are collected with the light oil. Moreover the light oil is discoloured by heavy oils adhering to the interior of the neck of the still from previous distillations. To secure comparable results, therefore, the fractions must be redistilled.

Accordingly the light oil, dried over calcium chloride, is redistilled up to 170° C. in an ordinary distillation flask, the distillate being collected in a clean flask. To the residue in the distillation flask the next fraction is added, and the distillation continued up to 230° C., and so on, till all is redistilled. These distillates (except the light oil) should be collected back into the receivers used in the first distillation, to avoid losing the adherent oil. The final residue is weighed as pitch.

Each fraction is now washed :—

(1) With 10 per cent. solution of sulphuric acid, to remove pyridine bases.

(2) With 10 per cent. of its volume of concentrated sulphuric acid, to remove unsaturated compounds, sulphur compounds, etc.

(3) With 10 per cent. of its volume of caustic soda solution (S.G. 1·1) to remove tar acids.

It is best to filter off naphthalene and anthracene by use of a Büchner funnel before washing. They are pressed down as tight as possible, to remove oil, and washed on the filter with acid and alkali. A further yield of anthracene can be obtained by redistilling the filtered oil.[1]

The oils, etc., are finally washed with water and the loss on washing noted. The washing (2) is usually rejected, but a little oil may be recovered from it by steam distillation. Pyridine bases are recovered from (1) by adding saturated caustic soda solution and salting out. The bases float to the top and are separated and measured. A small quantity may be estimated by distillation and titration. Tar acids are recovered from (3) by neutralisation with sul-

[1] This appears to indicate a pyrogenetic formation of anthracene during the distillation.

phuric acid and saturation with common salt. The separated acids are measured. The washed naphthalene and anthracene are dried as far as possible by the filter pump, and weighed as crude naphthalene and anthracene respectively. Gramme samples of each are taken for determination of the percentage purity.

The twisting point of the pitch (*see* Spielmann and Petrie, *J.S.C.I.* 1919, **38**, 58) is also taken. For this purpose two tin moulds $1\frac{3}{4} \times \frac{3}{4} \times \frac{1}{2}$ in. are filled with molten pitch, which is allowed to set. The blocks of pitch are then melted out by cautious warming of the moulds with a Bunsen burner. Each block is scraped down with a knife to a size of $1\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$ in. A copper wire (17 gauge) is bent at right angles $\frac{3}{4}$ in. from one end. The bent part is heated and then run through a pitch block perpendicular to two long sides, $\frac{1}{2}$ in. from one end of the block and equi-distant from the four long edges. The wire is supported so that it hangs vertical while the pitch block is horizontal. After remaining for a few hours the pitch is heated in a water bath at the rate of 1° C. per minute, and as the pitch softens the heavier end sinks. The temperature at which the upper angle of the pitch just reaches the vertical wire is taken as the softening point (FIG. 11A).

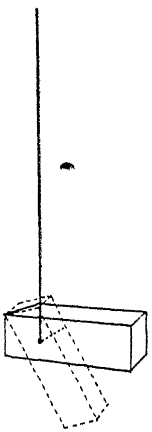

FIG. 11A.—SOFTENING-POINT OF PITCH.

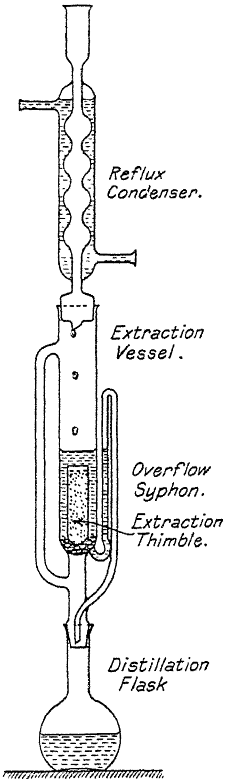

FIG. 11.—SOXHLET EXTRACTION APPARATUS.

ESTIMATION OF NAPHTHALENE AS PICRATE

Naphthalene reacts with picric acid to form an insoluble picrate $C_{10}H_8.C_6H_2(NO_3)_3OH$. It thus behaves like a

monoacid base of equivalent 128. Saturated picric acid solution is used for the determination; this is approximately $\frac{N}{20}$. It is standardised against $\frac{N}{20}$ $\left(\text{or at need } \frac{N}{10}\right)$ caustic soda solution, using lacmoid (or in default phenolphthalein) as indicator. A considerable amount of lacmoid should be used. 0·3 gramme of crude naphthalene is weighed out into a stout round-bottomed pressure flask and 50 c.c. of picric acid added. The flask is fitted with a rubber cork through which a sealed glass tube having a lateral opening passes so that the opening is inside. The opening allows the flask to be exhausted by a filter-pump. This done, the tube is drawn out of the flask until the opening is in the cork; it then acts simply as a plug.

The exhausted flask is heated for two hours in a water bath and allowed to stand overnight. It is then opened and the insoluble picrate filtered off and washed with a very little cold water. The excess of picric acid is then found by titrating the filtrate and washings with $\frac{N}{20}$ soda as before (1 c.c. $\frac{N}{20}$ solution = 0·0064 gramme naphthalene).

ESTIMATION OF ANTHRACENE AS ANTHRAQUINONE (Luck's test)

One gramme of crude anthracene and 45 c.c. of glacial acetic acid are placed in a litre R.B. flask provided with a reflux air condenser, and boiled until dissolved (FIG. 11). C.c. 23 of chromic acid solution (150 grammes CrO_3, 100 c.c. glacial acetic acid, 100 c.c. water) are then run in slowly from a dropping funnel resting loosely in the top of the condenser, the solution being kept boiling. The addition should take two hours, after which the mixture is boiled for two hours more and allowed to stand overnight. It is then diluted to 500 c.c. with distilled water, allowed to stand an hour, and the precipitated anthraquinone filtered off and washed :—

(1) With 200 c.c. of cold water.

(2) With 300 c.c. of boiling water.

(3) With 300 c.c. of caustic soda solution, S.G. 1·0125.

(4) With 300 c.c. of boiling water.

The precipitate is washed into a tared basin, dried in the steam oven, and weighed. Ten times its weight of fuming sulphuric acid (S.G. 1·88) is added and the basin heated on the water bath for about 15 minutes till all the contents crystallise. The basin is then allowed to stand in a damp place overnight. In the morning 200 c.c. of cold water are added and the anthraquinone filtered off, washed, transferred to a tared basin, dried, and weighed exactly as before. The basin is gently heated to volatilise the quinone, and afterwards reweighed with the non-volatile residue. Difference gives the weight of anthraquinone; this multiplied by 85·6 gives the percentage of anthracene in the sample.

ESTIMATION OF CAUSTIC SODA REQUIRED TO REMOVE TAR ACIDS FROM OILS

C.c. 100 of the oil to be washed are placed in a stoppered measuring cylinder, into which is run, a little at a time, caustic soda solution of the working strength, shaking well after each addition. When the last addition does not further diminish the volume of the oily layer, the extraction of the tar acids is complete, and the volume of soda solution required for this purpose should be noted.

FREE CARBON (Tar)

C.c. 100 of the tar are diluted with sufficient crude benzol (filtered if necessary) to make a mobile liquid. The carbon can then be filtered off, using a tared Gooch crucible, and weighed. It should then be transferred to the thimble of a Soxhlet extraction apparatus, and dealt with as described under Pitch.

FREE CARBON (Pitch)

Ten grammes of powdered pitch are weighed out into the thimble of a Soxhlet extraction apparatus, and extracted 50 times with

(*a*) 90's benzol.

(*b*) pyridine bases (90 per cent. at 140° C.) carefully dried over caustic soda.

(*c*) methylated spirit (industrial, free from paraffin).

The residue is then dried at 100° C. and weighed. For very accurate work the thimble should be treated with the solvents before use.

TAR ACIDS: WATER AND CRYSTALLISING POINT

Lowe's method is usually employed in this determination. C.c. 100 of the tar acids are placed in a long-necked 8 oz. retort and carefully distilled so as to avoid loss by uncondensed vapours, the distillate being collected in measuring cylinders. The first fraction contains all the water (up to 15 c.c.) with 10 c.c. of acids.

The next 62½ c.c. are collected in a fresh receiver, and are used to determine the crystallising point. The best method is to cool it in a freezing mixture until it is nearly all solid. Then remove it and gradually allow it to melt, stirring with a thermometer, and note the temperature at which the last traces of solid disappear. Subtract 2·5° C. from this to give the crystallising point at which the whole is solid.

The distillation should take about two hours. In collecting the first fraction the retort neck should be warmed towards the close to remove any adhering water. If x° F. is the crystallising point, the amount of "60's carbolic" (c.p. 60° F.) is calculated by the formula $\frac{x}{60} \times 100$.

CREOSOTE OIL: DISTILLATION

This is carried out in a retort as described under Allen's crude benzol test (page 46). The volume of distillate is measured at 200° C., 230° C. and 300° C. The water is contained in the first fraction, from which it separates and is measured. Until all the water is expelled the distillation must be conducted with the utmost care, very slowly over a moving flame. The face should be kept away from the retort as much as possible, and it is desirable to wear a

pair of goggles during the distillation to protect the eyes should the retort burst.

A good wash oil should give :—

0 per cent. up to 200° C.
5 per cent. up to 230° C.
90 per cent. up to 300° C.

The density at 15° C. should not be less than 1·020, and the crystallising point (*see* Tar Acids) not higher than 45° F. Naphthalene may be estimated by heating 20 c.c. of the oil with standard picric acid solution as previously described for solid naphthalene (page 66).

PYRIDINE

The only reliable method of estimating water in pyridine is to dry a measured volume by means of solid caustic soda and measure the residual volume. Shaking with strong soda solutions gives low results.

The pyridine is distilled in a distillation flask and the percentage distilling below 140° C. noted ; 90 per cent. is a standard quality. The first 10 c.c. of distillate may be tested for oil by dilution with water ; this dissolves pyridine and leaves any oil, which causes a turbidity.

The percentage of actual pyridine present is found by drying the sample over solid caustic soda, and distilling it up to 130° C., using a fractionating column (preferably a 5-bulb Young dephlegmator). Any distilling below 115° C. must be redried, and put back into the distillation flask with the residue and redistilled.

The distillate is a mixture of all the pyridine present (b.p. 115° C.) with some α picoline (b.p. 129° C.). The mean molecular weight is found by titrating 2 grammes with normal acid, using methyl orange or congo red as indicator. A little ferric chloride solution may also be used as indicator, acid being added till the ferric hydroxide first precipitated just dissolves on vigorous shaking (the ferric chloride solution should first be treated with pyridine till a permanent precipitate forms, and then filtered).

The molecular weight is $\frac{1000}{2 \times \text{c.c. acid used}}$. Pyridine has a molecular weight of 79, and picoline of 93, so that the relative weights of each present in the distillate are easily calculated. Thus if x is the molecular weight found, $\frac{\text{Pyridine}}{\text{Picoline}}$

$$= \frac{93-x}{x-79}.$$

CHAPTER VII

COAL ASH

COAL ash differs from the mineral matter associated with coal in the following respects :—

(1) It does not contain the water of crystallisation or of constitution of such minerals as gypsum $CaSO_4.2H_2O$ and clay $Al_2O_3.2SiO_2.2H_2O$. This water increases the hydrogen found by the combustion of the coal and in certain cases, with coals high in ash, the error may be appreciable. The analysis of the ash gives some idea of the amount of this water, but an accurate determination is impossible.

(2) Instead of calcium, magnesium and ferrous carbonates, the ash contains the corresponding oxides :—$CaCO_3 = CaO + CO_2$.[1] This carbon dioxide increases the carbon found by combustion of the coal. It can be estimated by treating the coal with dilute acid and passing the carbon-dioxide evolved into decinormal baryta-water. The last traces of carbon dioxide are expelled by boiling the acid and passing air free from CO_2 through it. The excess of baryta-water is then titrated (avoiding exposure to air) with standard $\frac{N}{10}$ oxalic acid, using phenolphthalein as indicator. Difference gives the baryta-water neutralised by the carbon-dioxide (1 c.c. = 0·0022 gramme CO_2).

(3) Ferrous iron is oxidised to ferric iron by the air : *e.g.* $4FeCO_3 + O_2 = 2Fe_2O_3 + 4CO_2$.

[1] CaO may be reconverted into $CaCO_3$ by moistening the ash with ammonium carbonate solution and reigniting it for a short time below a visible red heat.

This may be useful with coals containing much $CaCO_3$, as those of the Kent Coal Field ; also with mine road dusts in which limestone has been used as a "stone-dust."

(4) Iron pyrites is converted into ferric oxide and sulphur dioxide $4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$.

(5) Sulphur dioxide, from the pyrites and from the organic sulphur compounds of the coal, is retained to a varying extent by the lime and magnesia (formed chiefly from the carbonates) in the form of sulphates :—
$2MgO + 2SO_2 + O_2 = 2MgSO_4$.

For this reason the ash content of the coal will be found to vary slightly according to the manner of heating, a higher percentage being invariably found by combustion in oxygen (as in the ultimate analysis) than by the ordinary method.

To determine the various forms of sulphur in coal the following methods may be used (Powell & Parr, Univ. of Illinois, Bull. 111) :—

Five grs. of coal are digested with 300 c.c. of 3 per cent. HCl at 60° C. for 40 hours : the solution contains all the sulphur that exists in the coal as sulphate, together with part of the non-pyritic iron.

The residue is then treated at room temperature for 4 days with dilute nitric acid (1 vol. conc. acid + 3 vols. water) : the pyrites passes completely into solution and may be estimated by determining the iron and sulphur in the extract, which should be equivalent (regarding pyrites as FeS_2, $Fe \times 1{\cdot}145 = S$).

The organic sulphur is found in the residue, together with the silicate iron. As a check, the total iron and sulphur in the original coal should be found.

Powell recognises two groups of organic sulphur compounds, "resinic" and "humic" [1] : the former is estimated by extracting 0·5 grm. of coal with 25 c.c of phenol for 20 hours at 140° C., afterwards filtering quickly through a Gooch crucible, and washing the residue with alcohol and ether : the "resinic" sulphur is the sulphur in the phenol extract : it is more convenient, however, to determine the

[1] These terms are inappropriate.

sulphur in the residue and get the "resinic" sulphur by difference.

To determine the "humic" sulphur 5 grs. of coal are treated at room temperature for 24 hours with concentrated nitric acid: the residual "coal-acid" after washing is dissolved in 25 c.c.s of concentrated alkali, and the solution filtered. The filtrate is acidified with hydrochloric acid and the reprecipitated "coal-acid" analysed for sulphur.

The sum of the "humic" and "resinic" sulphur should nearly equal the total organic sulphur.

N.B.—The accuracy of the pyrites estimation could probably be increased, especially in coals low in ash, by concentrating, say, 200 grs. of coal, finely powdered, by floatation in a liquid of sp. gr. about 3·0. In this the bulk of the clean coal (sp. gr. about 1·3), shale (sp. gr. 2·2), gypsum (sp. gr. 2·6), etc., would float, while particles containing only 50 per cent. of pyrites (sp. gr. 5·0) would sink. The sinkings could then be analysed as indicated above. Suitable liquids would be methylene iodide, and saturated aqueous solutions of lead perchlorate, potassium mercuric iodide or barium mercuric iodide: the coal should first be moistened with alcohol and then stirred with the liquid used, in a large jar which is then filled to the brim: after standing overnight the floating coal is carefully skimmed off with a bent spoon: it is well to stir the residue with more liquid and repeat the separation. The liquid is then decanted and the residue filtered, washed and weighed.

FUSIBILITY OF ASH

This may be tested by grinding up the ash with a little water and moulding it into a pyramid like a Seger cone. When dry this is heated in a muffle furnace, and the temperature at which softening occurs (if attainable) noted. Highly ferruginous ashes usually melt at comparatively low temperatures, and so form clinkers in furnaces, etc.

COMPLETE ANALYSIS OF COAL ASH

SOLUTION OF THE ASH

One gramme of ash is intimately mixed with about 8 grammes of anhydrous sodium carbonate in a platinum crucible, which is covered and heated to bright redness in a muffle furnace, so as to fuse the contents. After half an hour the crucible is withdrawn and plunged into a dish of cold water; the rapid cooling causes the contents of the crucible to crack away from the metal. A green-coloured "cake" shows the presence of manganese. A little water is added to the crucible, which is then warmed on a hot plate or in a steam-oven. When loose, the cake is transferred to a 250 c.c. porcelain (or better, platinum) evaporating basin and treated with boiling water until it is quite disintegrated. About 150 c.c. of water should be used. The dish is then covered with a large clock glass, and concentrated hydrochloric acid (20 c.c. should suffice) added gradually from a pipette until all the sodium carbonate is neutralised. Some of the acid should be used to rinse out the crucible.

SEPARATION OF SILICA

The solution is evaporated to dryness on a hot plate, care being taken to avoid spurting. If the dish cannot be watched a steam-bath should be used. The dry residue is further heated until there is no smell of acid. The residue is moistened with concentrated hydrochloric acid and stirred up with hot water. Silica remains insoluble and is filtered off through an "ashless" filter paper, and washed free from chlorides with boiling water. A few drops of the final wash water should give no turbidity with silver nitrate solution. The precipitate is ignited wet in a tared platinum crucible and weighed. The crude silica is moistened with a few drops of concentrated sulphuric acid, and hydrofluoric acid is then added drop by drop, until the crucible is about one-third full. The liquid is

evaporated almost to dryness on a hot plate in a good draught. A little more hydrofluoric acid is then added and the evaporation completed. The crucible is ignited and weighed. The loss in weight gives the weight of silica.

PRECIPITATION OF ALUMINA, ETC.

To the filtrate from the silica (in a 400 c.c. beaker) add 10 c.c. of 10 per cent. ammonium chloride solution and a little bromine water. Boil, and add strong ammonia solution, drop by drop, with stirring, until the liquid smells permanently of it. Filter at once, using two filter papers if the precipitate is very bulky, and wash the precipitate well with hot water. Then re-dissolve it in boiling dilute hydrochloric acid (collecting the solution in the original beaker), dilute the solution to about 200 c.c., and reprecipitate and wash as before.

Boil down the combined filtrates and washings to a small bulk; add a few drops of bromine-water, and ammonia until alkaline; filter off any further precipitate through a small filter paper, and wash it well. Ignite it, and the main precipitate, in the platinum crucible containing the residue from the silica, and weigh as $Al_2O_3 + Fe_2O_3 + TiO_2$, etc. Fuse the precipitate carefully with six times its weight of potassium bisulphate and take up the melt with dilute sulphuric acid. Do not boil, or titanium may be precipitated. Filter off any silica that remains insoluble through a small filter paper, wash it, and ignite and weigh it as before. Test its purity with hydrofluoric acid as indicated. Make up the solution to 250 c.c. and take parts for the determination of iron, etc. The alumina is determined by difference.

IRON

C.c. 25 of the solution are diluted to 250 c.c., and 5 c.c. of this dilution measured into a Nessler glass; 5 c.c. of 10 per cent. potassium thiocyanate solution and 20 c.c. of water are added. The resulting red colour is matched by adding to a second Nessler glass containing equal quan-

tities of thiocyanate and water, a standard iron solution containing 0·000005 gramme Fe_2O_3 per c.c., made by diluting 1 in 20 a stock iron alum solution (0·63 gramme alum and 5 c.c. concentrated sulphuric acid per litre). If between 3 and 4 c.c. of standard solution are required all is well; otherwise a fresh comparison should be made, using a different dilution of the test solution, so as to bring the amount of standard solution required within these limits. When the colours match the iron contents of test and standard are equal. Hence the total iron is readily calculated.

Titanium

To 50 c.c. of the solution, in a Nessler glass, add 5 c.c. of concentrated sulphuric acid and 5 c.c. of 20 vol. hydrogen peroxide. A yellow colour shows the presence of titanium, which is very seldom absent; if the colour is brown, less solution should be taken and diluted to 50 c.c. The colour is matched, just as in the case of iron. The standard solution contains 1 gramme of TiO_2 (dissolved with the help of bisulphate) per litre.

Manganese

To 50 c.c. of the solution add just sufficient ·2 per cent. silver nitrate solution to precipitate any chlorides present. Filter off the silver chloride and add 10 c.c. more of the silver nitrate solution. Add 1 gramme of ammonium persulphate, boil and allow to cool. A pink colour shows the presence of manganese. Transfer to a Nessler glass and match the colour by adding to distilled water $\frac{N}{10}$ permanganate solution (1 c.c. = 0·00142 gramme MnO).

Phosphorus

To 100 c.c. of the solution (which may include the residue from the titanium estimation), add ammonia till alkaline, and boil down to 50 c.c. Add strong ammonia till a permanent precipitate just forms, then add 3 c.c. of concentrated nitric acid and 5 grammes of ammonium nitrate. Heat to 70° C. and rapidly add 20 c.c. of ammonium

molybdate solution (34 grammes per litre). Keep at 70° C. for half an hour (longer, if no precipitate separates), and then pour off the supernatant liquid through a small filter paper. Wash the precipitate, as far as possible by decantation, with 10 per cent. ammonium nitrate solution acidified with nitric acid (1 vol. conc. acid to 4 vols. ammonium nitrate). Dissolve the precipitate in the minimum quantity of $2\frac{1}{2}$ per cent. ammonia solution (poured through the filter on to the bulk of the precipitate). Acidify with acetic acid, and add a little ammonium chloride solution. Then add lead acetate solution, drop by drop, till no further precipitate falls. Filter and wash the precipitate with 2 per cent. ammonium acetate solution; ignite it, in a porcelain crucible, and weigh as lead molybdate $PbMoO_4$ ($24\ PbMoO_4 = P_2O_5$, or 1 gramme = 0·0161 gramme P_2O_5).

CALCIUM

Any calcium carried down with the alumina (say, by the presence of ammonium carbonate in the ammonia) may be detected by adding to a portion of the solution twice its volume of absolute alcohol and allowing it to stand overnight. Calcium sulphate is precipitated, and after filtration and washing with alcohol may be weighed, or better dissolved in water and estimated as described under water analysis.

SULPHATES

The filtrate from the alumina is made up to a convenient volume and sulphates determined in an aliquot part in the usual manner with barium chloride (1 gramme $BaSO_4$ = 0·343 gramme SO_3).

LIME

The rest of the filtrate is boiled and saturated ammonium oxalate solution is added. The precipitate is then allowed to settle out overnight. If large, the precipitate should be dissolved in the minimum amount of dilute nitric acid (after well washing with boiling water) and reprecipitated

as before. It is ignited and weighed as CaO (as quickly as possible, to avoid hydration of the lime).

A small precipitate is best dissolved and titrated with permanganate, as described under WATER ANALYSIS.

MAGNESIA

This is precipitated from the filtrate from the lime by the addition of ammonia and saturated sodium phosphate solution. The precipitate after standing overnight is filtered off, washed, ignited and weighed as $Mg_2P_2O_7$ (1 gramme = 0·362 gramme MgO).

Very small amounts are best determined turbidimetrically as described under WATER ANALYSIS. The filtrate from the magnesia determination is rejected.

ALKALIES (Lawrence Smith's method)

Fit a platinum crucible in a hole in a piece of asbestos so that only the bottom third projects. Charge the crucible in three layers with—

(1) 0·5 gramme calcium carbonate.

(2) 0·5 gramme ash, 0·5 gramme ammonium chloride, 3 grammes calcium carbonate, intimately mixed.

(3) 1 gramme calcium carbonate (with rinsings from mixing vessel). Heat the crucible over a very small flame till all the ammonium chloride is volatilised; then heat the bottom to dull redness for an hour. After cooling, add a little water and allow the crucible to stand; then transfer the contents to a large porcelain basin, add boiling water, and smash up the cake with a flat-ended glass rod. After keeping hot for half an hour filter and wash the residue thoroughly with boiling water. Reject the insoluble part. To the filtrate add ammonia and ammonium carbonate solution, boil, and filter off the precipitated calcium carbonate, which must be well washed by decantation with ammonia and ammonium carbonate. Evaporate the filtrate in a large porcelain basin, and heat the residue gently over

a moving flame to remove ammonium salts. Take up the residue with a little water, and slightly acidify with hydrochloric acid.

Boil the solution and add carefully barium chloride solution drop by drop as long as any further precipitate falls: only one drop in excess need be added. Keep the liquid hot until the precipitate has settled out, then filter it off and wash the precipitate.

To the filtrate add a little ammonia and ammonium carbonate and two or three drops of saturated ammonium oxalate solution, and allow it to stand overnight. Filter if necessary, evaporate and remove ammonium salts as before. Moisten the residue with strong hydrochloric acid and evaporate. Heat gently over a moving flame for a few minutes, cool and weigh as $NaCl + KCl$.

Potassium is now precipitated by the use of a solution of chloroplatinic acid containing 0·1 gramme of platinum (dissolved in aqua regia and evaporated several times with hydrochloric acid) per c.c. The quantity required (in c.c.) is seventeen times the weight in grammes of the mixed chlorides, + 0·3 c.c. This is added to a dilute solution of the mixed chlorides, which is then evaporated till syrupy and allowed to cool, when it should solidify.

The cake is treated with a little 80 per cent. alcohol and smashed up with a flat-ended glass rod. The alcohol is decanted through a tared filter, and more added, until the washings are colourless and the precipitate bright yellow. The precipitate is then transferred to the filter, dried at 130° C., and weighed as K_2PtCl_6 (1 gramme = 0·307 gramme KCl = 0·194 gramme K_2O).

The sodium is found by difference :—(1 gramme $NaCl$ = 0·530 gramme Na_2O). A blank experiment must be done on the reagents.

The foregoing methods apply equally to the analysis of refractory materials such as fire-clay. In this case the loss on ignition should also be found.

PARTIAL ANALYSIS OF COAL ASH

Very often a coal ash has only to be analysed for one or two constituents such as iron or phosphorus. In such cases the following more rapid method may be used:—

Fuse one gramme of ash with six grammes of potassium bisulphate in a platinum dish: take up the melt with dilute sulphuric acid, filter off the silica which separates (this may be weighed as usual), and make up the filtrate to 250 c.c.

The solution so obtained is treated just as the solution of the ammonia precipitate in the complete analysis, portions being taken for the estimation of titanium, iron, calcium, phosphorus as desired.

CHAPTER VIII

WATER ANALYSIS (FOR BOILERS AND WASHERIES)

TOTAL SOLIDS

MEASURE 250 c.c. of water in a measuring flask. Carefully weigh a small porcelain basin, previously dried and cooled in a desiccator. Fill it about three-fourths full from the flask, and evaporate on a water-bath. A large inverted funnel should be supported over the basin to minimise the entrance of dust. As the water evaporates more is added from the flask, and finally the latter is rinsed out with a little distilled water. When all the water is evaporated the basin is removed and the outside carefully wiped with a piece of cotton-wool soaked in dilute hydrochloric acid, to dissolve carbonates, etc., which may be deposited on it from water from the water-bath. After this, the outside of the basin is rinsed with distilled water, and dried with a clean cloth. The basin is finally dried in a toluene oven at 108–110° C. for thirty minutes, cooled in a desiccator, and weighed.

If the residue is very hygroscopic it is best to begin the weighing while the basin is still just warm. After weighing, the basin is replaced in the oven for fifteen minutes, and then re-weighed as before, care being taken, however, to have all the weights ready on the balance-pan before the basin is removed from the desiccator, so that the weighing may be as rapid as possible.

SODIUM AND POTASSIUM

Take up the total solid residue carefully with a little cold water ; filter the solution and add baryta water, drop by drop, to the boiling filtrate until no further precipitate

falls. This precipitates magnesia and sulphates. Boil down to 10 c.c. and filter into a test-tube, washing the precipitate. Add ammonium carbonate solution drop by drop till there is no further precipitate, and then one drop of ammonium oxalate solution; this removes calcium and barium. Allow to stand for fifteen minutes and filter. Evaporate the filtrate and warm the residue gently with a Bunsen flame to expel ammonium salts. Take up the residue with a little dilute hydrochloric acid and transfer it to a small weighed crucible. Then evaporate to dryness and weigh as $NaCl + KCl$.

Dissolve the mixed chlorides in water, and determine the weight of chlorine in them as described under Chloride. Subtract this from the weight of the mixed chlorides, and the result is the weight of sodium and potassium, $Na + K$.

Do not attempt to estimate the relative proportions of sodium and potassium by this method, as small errors and traces of impurities render the result worthless. If the separate weights of sodium and potassium are required, the only reliable method is to separate by means of chloroplatinic acid (*see* page 79). The above result, however, is enough for most purposes.

The utmost care is essential in order to obtain a reliable result. The filter-papers must be no larger than absolutely necessary, and the minimum excess of reagents added. Note that the chlorides are appreciably volatile at red heat.

CALCIUM

Measure 200 c.c. of water into a 350 c.c. conical flask, and slightly acidify it with hydrochloric acid to prevent separation of calcium carbonate. Boil it gently on a hot plate till the volume is reduced to 50 c.c. For this purpose it is convenient to mark the flask roughly at 50 c.c. Examine the concentrated water carefully for turbidity, which would probably be due to calcium sulphate; if this is found the water is discarded and 50 c.c. of the original water used without concentration.

To the hot liquid add ammonia (1 : 4) till the water smells distinctly of it. Should any precipitate (magnesia) separate it may be dissolved by adding a little solid ammonium chloride. Add 2 c.c. of saturated ammonium oxalate solution and stand the flask on the hot plate for an hour. Filter off the precipitated calcium oxalate with a 5 cm. filter paper, and wash it with hot distilled water until the (hot) wash water, after being acidified with dilute sulphuric acid, does not decolorise a drop of $\frac{N}{100}$ permanganate solution. Keep the filtrates and washings for the estimation of magnesium.

The precipitate is now redissolved in a few drops (no more) of dilute hydrochloric acid, which may be poured repeatedly through the paper. The solution is collected in the conical flask in which the precipitation was made, and which may still contain a little of the precipitate adhering to the sides. The paper should be well washed with hot water and finally with sufficient dilute sulphuric acid to make the solution strongly acid. It is not advisable to perforate the filter paper and rinse the precipitate into the flask, as it is then very difficult to avoid introducing shreds of filter paper into the solution.

The hot solution is titrated with $\frac{N}{100}$ permanganate solution to a permanent pink colour. If the solution goes brown, add more sulphuric acid. Subtract from the volume of permanganate used that required to give an equal pink colour to the same volume of distilled water. Each c.c. of permanganate corresponds to 0·0002 gramme of calcium. In some cases $\frac{N}{10}$ permanganate may be needed.

MAGNESIUM

This is determined in the filtrate from the calcium determination, which is made up to 100 c.c. (or boiled down to that volume; in the latter case, however, far too much

wash water will have been used in the calcium estimation). The amount of solution required for the determination depends on the amount of magnesium present: if the calcium does not exceed 2 grammes per 100,000 c.c. of water, the whole of the filtrate may be used, otherwise an aliquot part (with 8 parts of calcium 1/4, and so on), is taken and made up to 100 c.c. Do not throw away the rest of the filtrate.

A standard magnesium sulphate solution, containing 0·25 gramme of magnesium per litre, is now required. It may be made by dissolving the required weight of magnesium ribbon in a little acid and diluting to a litre: 5, 10 and 15 c.c. of this are taken, each lot being made up to 100 c.c. These standards, with the solution for testing, are placed in 200 c.c. stoppered bottles, carefully labelled. To each is added 2 c.c. of 0·880 ammonia and 2 c.c. of saturated sodium phosphate solution. They are then allowed to stand half an hour, being well shaken at intervals. The magnesium is estimated by comparing the turbidity of the test solution with that of the standard with which it most nearly corresponds.

The comparison is effected in a 100 c.c. measuring cylinder, carefully selected for the clearness of its glass. This is placed, in a steady light, on a small piece of paper ruled with pencil lines; several such pieces, with lines of varying thickness to suit varying turbidities, should be provided. The test liquid is poured in until, looking down the cylinder, the pencil lines are just obscured; the volume is then read, and the turbid liquid drained back into the bottle. The same process should be repeated with the standard. The turbidities of the two solutions, and their magnesium contents, will be inversely as the volumes required to "extinguish" the lines.

For an accurate comparison neither volume should be less than 50 c.c., and they should not differ by more than 5 c.c. (The mean of several readings must be taken, without changing the position of the cylinder. Care should also

be taken to adjust the volumes before any noticeable settling occurs.) From the first results it is easy to calculate what quantities of test and standard solutions are required for this. A fresh portion of the original filtrate is diluted, and a fresh standard made up, and both are precipitated together, and compared as before. Where all the filtrate is used in the first comparison, that from a duplicate calcium estimation may be used or, if this is not convenient, a fresh standard only may be made up, and allowed to stand for several hours, instead of only half an hour. In this way precipitation is practically complete in both test solution and standard, whereas in the shorter method it is incomplete to about the same extent in both.

Where the whole filtrate does not give enough turbidity to extinguish the faintest pencil lines, it must be compared with the standard as well as possible by noting the dimness of the lines as seen through the liquids. The diminished accuracy is of little importance in this case, as the total quantity is so small.

CHLORIDE

Measure out into each of two large porcelain basins 200 c.c. of water, and to each add 2 c.c. of 5 per cent. potassium chromate solution. Titrate one with $\frac{N}{10}$ or $\frac{N}{100}$ silver nitrate solution (according to the amount of chloride present) using the other dish as a comparison. The change is from pure yellow to a reddish-brown colour. Titrate back with the water, running in 1 c.c. at a time, until the yellow colour is restored; add half the volume of the water required to do this to the original 200 c.c., in calculating the result. Now titrate the second dish in exactly the same way, using the first dish as a comparison; the comparison will be better than in the first titration, owing to the presence of silver chloride in the comparison dish. If the titrations agree fairly well, the second may be taken as correct, otherwise further titrations should be made.

In this titration strong sunlight must be avoided. It is important not to add less indicator than stated. If the volume is much increased by the addition of silver nitrate solution, a further proportionate quantity of potassium chromate should be added. A fine suspension of silver chloride selectively scatters white light, with the result that it appears bluish by reflected and golden-brown by transmitted light. The latter colour must be masked by titrating in opaque dishes and adding plenty of indicator, otherwise a premature end-point will be taken.

One c.c. of $\frac{N}{10}$ silver nitrate solution is equivalent to 0·00355 gramme chlorine. It contains 17 grammes per litre and is standardised against $\frac{N}{10}$ salt solution (5·85 grammes per litre), by the above method. The salt solution is made up by weighing the required amount of pure dry salt.

NITRATE

This estimation need only be made to complete the mineral analysis of a water, when it is desired to see whether the sum of the constituents found agrees (roughly) with the total solids, and whether the acidic and metallic radicles are equivalent.

A 100 c.c. conical flask is taken and sufficient granulated zinc added to cover the bottom. This is washed, first with dilute sulphuric acid (1 : 4), then with distilled water. It is then covered with distilled water and 2 c.c. of saturated copper sulphate solution added. After standing a few minutes the liquid is poured off, and the zinc-copper couple thus prepared is washed very carefully with distilled water so as not to disturb the coating. C.c. 25 of the water are added, and one drop of dilute hydrochloric acid. The flask is then closed by a cork fitted with an outlet tube closed by a Bunsen valve. It is placed in a warm place (*e.g.* the top of the steam ovens) for one hour, acid being added as required to maintain a barely perceptible evolution of hydrogen. The nitrate is reduced to ammonia.

Meanwhile in a room free from ammonia fumes an ammonia distillation apparatus (*see* AMMONIA LIQUOR, page 40), is set up, the flask being half full of dilute caustic soda solution —a 1 per cent. solution will suffice for many successive distillations. This is distilled until 50 c.c. of the distillate collected in a Nessler cylinder gives no perceptible colour with Nessler's solution after standing five minutes. It is then allowed to cool.

The contents of the flask are now poured into the distillation apparatus, the couple being rinsed with ammonia-free distilled water. Great care should be taken to prevent the entry of zinc into the distillation apparatus, as this would reduce nitrates present in the caustic soda and vitiate the results. The liquid is distilled and the distillate collected in 50 c.c. fractions in Nessler glasses as long as any ammonia comes over. The ammonia in the distillates is estimated by comparison with standard ammonium chloride solution, containing 0·025 gramme NH_3 per litre, made up as required by diluting a stock solution 100 times as strong, containing 7·87 grammes NH_4Cl per litre. Ammonia-free water must be used for the preparation and dilution. A few c.c. of this solution is diluted to 50 c.c. to form the standard. To both standard and test solutions 2 c.c. of Nessler's solution are added, and the yellow colours compared. For accurate matching the colours should not appear immediately, but only on standing a minute or two. Yellow, not brown, colours should be aimed at. To secure this it is frequently necessary to dilute the first 50 c.c., hence it is advisable to nesslerise the second 50 c.c. fraction first. If this contains much ammonia, the first fraction should be diluted, and a part only nesslerised.

Matching is effected by making up standards equal in colour to the distillates by the method of trial and error. Freshly made up standards must be used, unless a set of permanent standards is made by using some less fugitive colouring matter, such as iodine solution. With practice the colour of the distillate will suggest the volume of standard

solution required; a little time spent in making up and comparing standards before the distillation will considerably assist rapid comparison. If standard and test solutions are nearly alike, a little liquid may be poured out of the darker glass, until, looking down the columns, the colours match. The ammonia contents will then be inversely as the lengths of the liquid columns.

Ammonia-free water is obtained by re-distilling water, rejecting the distillate as long as Nessler's test shows the presence of ammonia. The residue may then be used, or preferably the distillation is continued, ammonia-free water being collected.

Nessler's solution is made as follows :—

Dissolve 35 grammes of potassium iodide in 100 c.c. of water, and add cold saturated mercuric chloride solution until the red precipitate is nearly re-dissolved. Add 120 grammes (six sticks) of caustic soda and dilute to 1 litre; then add a little more mercuric chloride solution to give a permanent red precipitate, and allow it to settle. For use it is carefully pipetted off from the sediment. It improves with keeping, provided a little mercuric chloride solution is added from time to time. Ammonia-free water is not necessary for this preparation.

As described, free ammonia and nitrites in water would be estimated as nitrates. If not separately estimated, the free ammonia can easily be boiled off before reduction; the correction is usually small. Nitrites, if present at all, are present in such small quantities that it is not worth while to estimate them simply for the purpose of correcting the nitrate figure.

One c.c. standard solution = 0·000025 gramme NH_3 = 0·000091 gramme NO_3.

SULPHATE

This may be determined turbidimetrically just as in the case of magnesium, 100 c.c. of the water, or of a known dilution of it, being precipitated in the cold with 2 c.c. of

10 per cent. hydrochloric acid and 2 c.c. of 10 per cent. barium chloride solution. As a standard $\frac{N}{10}$ or $\frac{N}{100}$ sulphuric acid may be used; this method is very convenient for rapid work, and also for practice in turbidimetric estimations generally.

A convenient volumetric method is as follows :—Barium chromate is prepared by precipitation of 1 gramme of barium chloride with its own weight of potassium chromate, in ammoniacal solution. The precipitate is well washed, dissolved in the minimum quantity of 10 per cent. hydrochloric acid, and made up to 200 c.c. C.c. 100 of the water is boiled in a beaker, and 2 c.c. of this solution added, drop by drop. The solution is kept hot for an hour; barium sulphate is precipitated and an equivalent quantity of other chromates formed. Ammonia is then added; this precipitates the unchanged barium chromate. The liquid is kept hot until the mixed precipitate has settled and is then filtered. The filtrate should be yellow owing to the presence of chromates equivalent to the sulphates. The filtrate is made just acid with hydrochloric acid; 1 c.c. of 1 per cent. potassium iodide solution is added, and the liberated iodine titrated with $\frac{N}{100}$ thiosulphate solution, using starch solution as indicator, the end point being the disappearance of the blue colour. The thiosulphate should be standardised against 20 c.c. of $\frac{N}{100}$ sulphuric acid, treated in exactly the same way as the water under examination.

It will usually be found that the blue colour returns to the titrated liquid after standing ten minutes or so. This is due to the catalytic atmospheric oxidation of the hydriodic acid in presence of traces of nitrous acid (or manganic salts) in the water or laboratory air, and may be neglected. If the "after blueing" causes serious difficulty in titration, the best thing to do is not to titrate, but to estimate the chromate by comparison of the colour with $\frac{N}{10}$ potassium

chromate solution, suitably diluted. The comparison is carried out in Nessler glasses as described under Nitrate. If a difference in tint causes trouble, both solutions should be acidified with hydrochloric acid; this converts the yellow chromates into orange dichromates, and usually reduces the difference. The $\frac{N}{10}$ chromate solution may be standardised against $\frac{N}{10}$ sulphuric acid by the same method.

One c.c. $\frac{N}{100}$ thiosulphate or chromate solution is equivalent to 0·00048 gramme SO_4.

CARBONATE, BICARBONATE AND HYDROXIDE

C.c. 200 of water is titrated against $\frac{N}{100}\left(\text{or } \frac{N}{10}\right)$ sulphuric acid using methyl orange (1 gramme per litre of water) as indicator. Each c.c. of acid corresponds to 0·0003 gramme CO_3, equivalent to 0·0005 gramme $CaCO_3$; calculated as calcium carbonate, the figure should roughly agree with the temporary hardness, unless sodium carbonate is present (when the alkalinity is retained after boiling and filtration), as in waters softened by the use of Permutit, which converts calcium salts into the corresponding sodium salts. Similar natural waters are also met with as various rocks, *e.g.* the Thanet sands, have a similar action.

The acid is standardised against $\frac{N}{100}$ sodium carbonate solution, 0·53 gramme per litre.

Sometimes it is desirable to distinguish bicarbonates from carbonates, or to detect and estimate hydroxides, as in water softened by the use of lime. (Note that bicarbonates and hydroxides cannot be simultaneously present.) In this case a titration using phenolphthalein as indicator is also made. If acid to phenolphthalein, only bicarbonates are present, together with free carbon-dioxide, which may be estimated by titrating back with $\frac{N}{100}$ sodium carbonate

solution (1 c.c. = 0·00022 gramme CO_2 = 0·00031 gramme H_2CO_3).

If alkaline to both indicators the two titrations may be combined; running in acid until the phenolphthalein is decolorised, then adding methyl orange and continuing the titration. Carbonates only require half as much acid to make them neutral to phenolphthalein as they do to make them neutral to methyl orange, which is unaffected by carbon-dioxide; this may be verified while standardising the acid. Hence

m = bicarbonate + carbonate + hydroxide.

p = $\frac{1}{2}$ carbonate + hydroxide.

Where m and p are the alkalinities towards methyl orange and phenolphthalein respectively, expressed in c.c. of $\frac{N}{100}$ acid. If $m > 2p$ hydroxides are absent and bicarbonates present, and the reverse obtains if $2p > m$.

The two equations are readily solved for carbonate, etc., in terms of standard acid:

1 c.c. $\frac{N}{100}$ acid = 0·00017 gramme OH (hydroxide).

= 0·0003 gramme CO_3 (carbonate).

= 0·00061 gramme HCO_3 (bicarbonate).

HARDNESS

This determination enables the suitability of a water for boiler use to be rapidly determined without making a complete analysis. A standard soap solution, containing 12 grammes of shredded castile soap per litre of methylated spirit (free from paraffin) is made up. After standing twenty-four hours, preferably in ice, it is filtered. Other soaps may be used if necessary. A standard calcium solution is made up by dissolving 2 grammes of selected crystals of Iceland spar in hydrochloric acid, evaporating to dryness to expel excess of acid, and diluting to a litre. Equivalent quantities of other soluble calcium or barium salts may be used.

To standardise the soap solution, take 5 c.c. of the calcium solution, dilute to 100 c.c., and transfer to a stoppered bottle; run in soap solution, 1 c.c. at a time, shaking vigorously after each addition, until, the bottle being laid on its side to give as big a liquid surface as possible, a lather persists unbroken on the surface for five minutes. The noise made by the solution on shaking changes at this point. The titration is now repeated, this time running in the bulk of the soap solution at once, and finishing by adding small quantities till the end point is reached. The method of adding the soap solution may make a considerable difference to the result; in final titrations it must nearly all be run in at once. C.c. 100 of distilled water are now titrated in the same way, the amount of soap solution required to give a similar lather in this case being deducted from the former reading and from all subsequent titrations. Usually it will be about 1 c.c. If the corrected volume of soap solution is 10 c.c., it is of the required strength, otherwise the strength must be adjusted and verified. The solution must be standardised every time it is used, a stock of stronger soap solution being kept for bringing it up to strength. As long as the solution remains clear, its strength is not much diminished.

To determine the hardness of a water, 100 c.c. are titrated against the standard soap solution, and the volume required noted. The quantity of water required for 10 c.c. of soap solution is then calculated, and this volume is taken, made up to 100 c.c. with distilled water, and titrated. If less than 10 c.c. of soap solution are required per 100 c.c. of water, it is titrated directly. The error in neglecting this dilution is not serious provided not more than 15 c.c. of soap solution is required.

The hardness is defined as the number of c.c. of soap solution required by 100 c.c. of the water, when titrated as above. It is expressed as parts of $CaCO_3$ per 100,000, as the standard calcium solution with which the water is indirectly compared contains the equivalent of a known

weight of calcium carbonate. To convert to grains per gallon (degrees Clark) multiply by 0·7.

Permanent hardness is estimated by titrating the water after boiling for thirty minutes, filtering, and making up to the original volume. The difference between the total and permanent hardness gives the temporary hardness, corresponding to the calcium and magnesium carbonates precipitated by boiling.

If much magnesium is present the end point is obscured by a curd of insoluble magnesium soap which forms on the surface. Copious dilution is the best remedy.

As already noted, temporary hardness may, with some waters, be calculated from the alkalinity, and the method is sometimes preferred on the ground that the end-point is sharper. In such cases the following method may be used to give the permanent hardness. C.c. 250 of water are boiled for ten minutes, 25 c.c. of $\frac{N}{10}$ soda solution (consisting of equal volumes of $\frac{N}{10}$ NaOH and $\frac{N}{10}$ Na_2CO_3) are added, and the solution boiled nearly to dryness, whereby calcium and magnesium are precipitated. The excess of soda is titrated with $\frac{N}{10}$ acid, using methyl orange as indicator, and the loss of alkalinity, calculated as before as $CaCO_3$, gives the permanent hardness. The precipitate may either be filtered off before titrating, care being taken to wash the paper free from alkali, or the whole may be made up to 250 c.c., left to settle, and 100 c.c. then pipetted off and titrated.

By using only $\frac{N}{10}$ NaOH (containing $Ba(OH)_2$ to precipitate carbonates, which are allowed to settle) only magnesia is precipitated.

The loss of alkalinity of the $\frac{N}{10}$ NaOH used then indicates the magnesium.

CALCULATION OF THE RESULTS OF A WATER ANALYSIS

Individual results are best calculated in terms of the acidic or basic radicals, *e.g.* K, Na, Ca, Mg, CO_3, SO_4, Cl, NO_3 ... rather than as the oxides K_2O, Na_2O, CaO, MgO, CO_2, SO_3, N_2O_5 ... as in this case there is a difficulty with the chlorine, which has to be regarded as partially replacing the oxygen in some of the oxides. The results are calculated, in the first instance, as grammes per 10^5 c.c.; multiplication by 0·7 converts them to grains per gallon.

Attempts are usually made to combine the radicals to give the compounds which will probably separate on evaporating the water, but this is a matter which obviously introduces an element of uncertainty. Probably for present purposes the best plan is :—

(1) Calculate the carbonate as $MgCO_3$.

(2) Calculate any excess of carbonates as $CaCO_3$. (Any remaining excess is alkali carbonate, but this is rare.)

(3) Calculate any excess of calcium as $CaSO_4$.

(4) Calculate the chlorine as alkali chloride NaCl + KCl (with the help of the weight of mixed chlorides in the alkali determination). Any excess of chlorine is to be assigned to magnesium, or in default to calcium.

(5) If the chlorine is not sufficient to satisfy the alkalies the defect is made up with nitrate, and if necessary with sulphate (and in rare cases carbonate).

(6) Any remaining sulphate is ascribed to magnesium, and any nitrate remaining is distributed between any calcium and magnesium left.

Note that if two radicals are nearly equivalent it is better to suppose the difference to be experimental error, and give the mean value, rather than to calculate a small quantity of another salt to use up the excess. The sum of the equivalents of $CaCO_3$ and $MgCO_3$ should be compared with the temporary, and of the other calcium and magnesium salts with the permanent hardness. If there is a large discrepancy the distribution should be modified, care being

taken in all cases not to under-estimate $CaSO_4$, which is the least desirable constituent.

ESTIMATION OF SOLUBLE SALTS IN COAL

100 grammes of coal is extracted with about 1000 c.c. of boiling water for one hour and filtered. The filtrate is made up to 1 litre and examined by the methods already given. Very often a chlorine titration is all that is required. The coal often retains salts very obstinately, and as a rule many repetitions of the above procedure will not give complete extraction. In some cases further extractions with dilute nitric acid may be made to dissolve out carbonates and more chlorides; in this case the chlorides may be estimated turbidimetrically without neutralising the acid.

CHAPTER IX

GAS ANALYSIS

COAL GAS (1)

GASES are usually analysed by volume. For coal gas, provided at least 100 c.c. is available, Hempel's mercury burette may be used (FIG. 12). This consists of a measuring tube A connected by pressure-tubing to a mercury reservoir B, a tap F being provided between A and B. By raising or lowering B the pressure A can be varied. F is closed when the desired pressure is obtained. A compensating tube C serves to eliminate the effect of variations of temperature and pressure. A manometer D permits the adjustment of the pressures in A and C to equality. A and C are surrounded by a common water-jacket. A three-way tap E allows A to be put into communication either with D or with an absorption vessel. This tap should be tested for leakage by reducing the pressure inside the burette, when no air should enter.

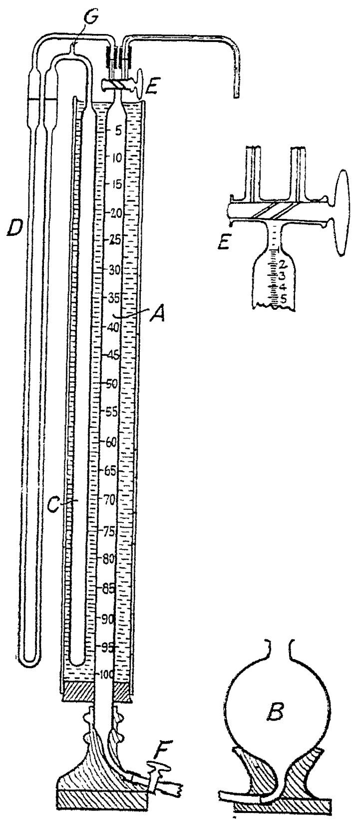

FIG. 12.—HEMPEL'S MERCURY BURETTE

It is necessary to determine the volume of the air-

space in D on the side adjacent to the measuring tube (about 2·5 c.c.). To do this A and D are put into communication, and by lowering B the mercury in D is sucked up as far as the tap. E is then reversed, and any volume of air drawn in and measured with E open (*i.e.* at atmospheric pressure). A and D are again put into communication and the manometer levelled (the other limb being temporarily open to the air at G). The air in A is remeasured, and the loss is the required volume. G should then be sealed, after which the burette is ready for use.

The gas for analysis may be collected in an ordinary sampling tube which is initially filled with water (or, in more accurate work, with mercury). On connecting the sample tube with a pipe from which the gas is issuing, and opening the taps, the water is displaced by the gas, and this is retained by closing the taps before detaching the vessel.

This vessel is attached to the open branch of E and any desired quantity drawn into A. It is best to use 100 c.c. (including the manometer space). The quantity is measured by putting A in communication with D, levelling the manometer, closing F and noticing the position of the top of the mercury meniscus in A, or preferably where the mercury touches the glass. If necessary more gas can then be drawn in, or *vice versa*, until the desired volume is obtained. Note that the gas is measured saturated with water-vapour throughout.

The various constituents are then withdrawn successively by suitable absorbents as shown in the table on the following page.

Note that alkaline pyrogallol will absorb carbon dioxide as well as oxygen. Similarly cuprous chloride will absorb oxygen as well as carbon monoxide. Hence the order given must be adhered to.

The absorbents are contained in pipettes, which are either single or double, the latter being used for pyrogallol and cuprous chloride, to prevent exposure to air.

Gas.	Absorbent.
Carbon-dioxide . .	Potash (1 pt. KOH to 2 pts. H_2O).
Olefines, benzenes, etc.	Fuming sulphuric acid, followed by potash.
Oxygen	Alkaline pyrogallol (5 pts. pyro in 15 pts. H_2O, 120 pts. KOH in 80 pts. H_2O).
Carbon monoxide . .	Acid cuprous chloride, followed by potash (25 pts. $CuSO_4 5H_2O$ + 12 pts. NaCl are dissolved in 50 pts. H_2O; add 100 pts. conc. HCl, 13 pts. copper turnings, and boil under reflux till colourless).

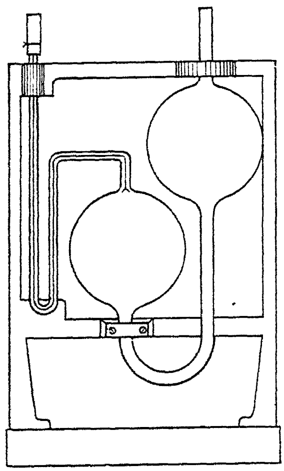

FIG. 13A.—HEMPEL'S SINGLE ABSORPTION PIPETTE.

For use the large bulb of the pipette must be completely filled with liquid. By tilting, the air in the capillary tube may be displaced and the pipette may then be connected to the measuring tube by a ⊓ shaped piece of capillary tubing. By raising B the gas is transferred to the large bulb of the pipette, the liquid flowing into the smaller bulb. The gas may now be shaken with the absorbent for some minutes, and then drawn back into A and remeasured, care being taken on each occasion to transfer the gas in the manometer to the pipette.

It is then advisable to repeat the treatment in order to make sure that absorption is complete. Special care must be taken to absorb the carbon-monoxide completely: this is done by a second treatment, using a pipette containing almost new cuprous chloride. Needless to say, the utmost care must be taken to avoid leakage.

The residual gas consists of methane, hydrogen and nitro-

gen, and is stored, after measurement, in a pipette containing dilute sulphuric acid, which is kept for the purpose.[1] C.c. 12 (or, with poor quality gas, 15 c.c.) are measured into the measuring tube, and enough air drawn in to make up the volume to nearly 100 c.c. After measurement the mixture is transferred to the explosion pipette, a mercury pipette provided with firing-wires and a stop-cock.

The pressure in the explosion pipette is reduced as much

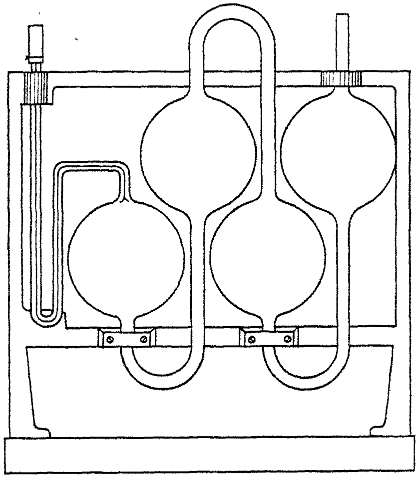

FIG. 13B.—HEMPEL'S DOUBLE ABSORPTION PIPETTE.

as possible by lowering the mercury reservoir. The tap is then closed and the mixture exploded by a spark from an induction coil. If the mixture will not explode the pressure in the pipette may be increased, and if possible a stronger spark used. If failure still results a richer mixture may be made up. If failure is again experienced, pure oxygen, which can be prepared by electrolysing baryta-water with silver electrodes, must be used instead of air. In some cases it may be necessary to add also to the measured mixture a

[1] The mercury in the burette should be rinsed with dilute sulphuric acid before making up the mixture: the joints with the explosion pipette must be securely wired.

quantity (not more than 25 per cent.) of electrolytic gas to secure an explosion.

After explosion the gas is again measured and the contraction noted. The carbon-dioxide formed by the explosion is then absorbed as usual. Finally the excess of oxygen is removed by pyrogallol, and the residual nitrogen measured; from this the nitrogen contained in the air used for combustion (79 per cent.) is deducted, leaving the nitrogen originally present which should agree closely with the nitrogen as found by difference.

The carbon dioxide formed by the explosion is equal in volume to the methane, as the following equation shows :—

$$\underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{2O_2} = \underset{\text{1 vol.}}{CO_2} + \underset{\text{(condensed).}}{2H_2O.}$$

The equation also shows that the contraction due to the methane is twice the volume of the methane. The remaining contraction is due to hydrogen, and is $1\frac{1}{2}$ times the volume of the hydrogen :—

$$\underset{\text{2 vols.}}{2H_2} + \underset{\text{1 vol.}}{O_2} = 2H_2O;$$

hence the hydrogen, methane and nitrogen may be calculated.

If the nitrogen, determined directly, does not agree with that found by difference the error is usually due to incomplete absorption of carbon-monoxide, provided there has been no leakage.

As only a part of the residual gas is taken for the explosion analysis, the error in measurement is multiplied in calculating the quantities as percentages of the original volume of gas. Hence the measurements must be made with great care, and the mean of several explosions taken.

COAL GAS (2)

A more accurate analysis of coal gas, or other gaseous fuel, may be made by means of Bone and Wheeler's apparatus (FIG. 14), which is specially useful when only a small quantity of gas (5 to 10 c.c.) is available. The pressure of the

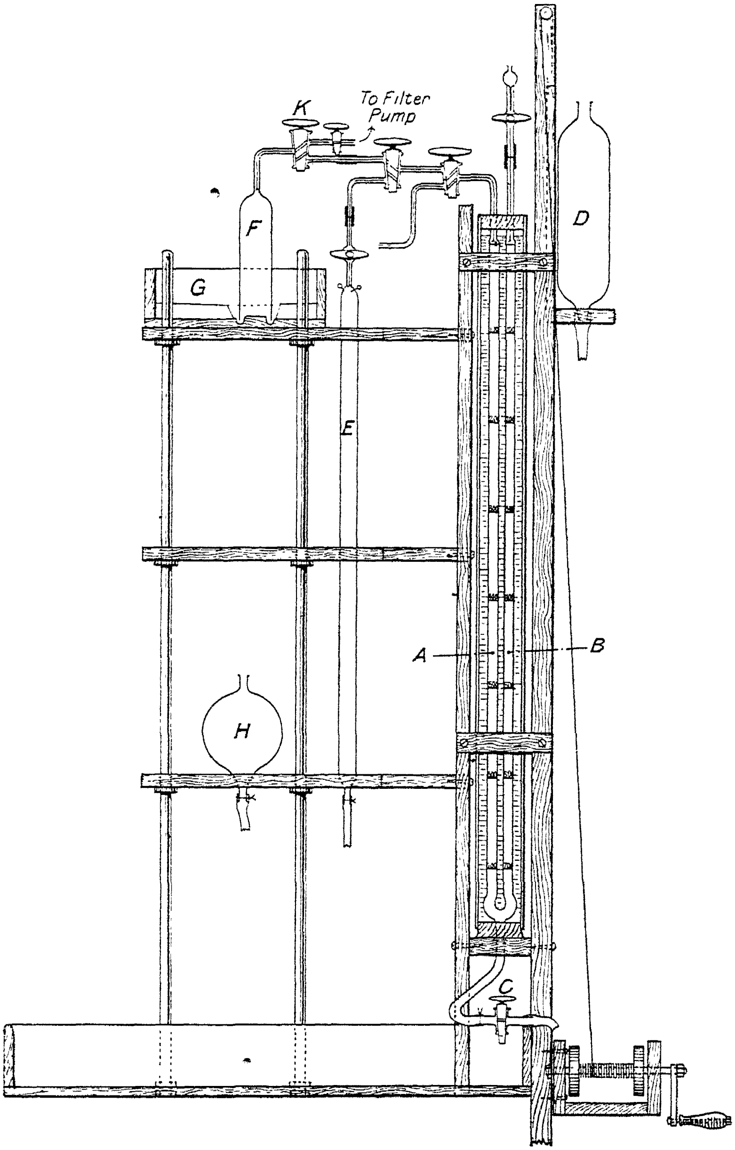

FIG. 14.—BONE AND WHEELER'S GAS ANALYSIS APPARATUS.

gas at constant volume is measured. The gas is contained in the measuring tube A, containing a series of "constant-

volume" marks, one of which is used throughout the analysis. The pressure at this volume is measured in the barometer-tube B, which is closed by a mercury sealed tap through which any gas may be expelled when fitting up the apparatus. The mercury level in A is adjusted by the reservoir D, the tap being closed when the adjustment is effected. A fine adjustment is easily made by compressing with a screw-clip the pressure tubing connecting C with A and B. Absorption is carried out in the vessel F standing in the mercury trough G, where also the gas sample may be introduced from an ordinary test-tube standing in a crucible of mercury. By the three-way tap K, F can also be put into communication with a filter-flask exhausted by a filter-pump, whereby used absorbents, etc., may be sucked out.

The absorbents are introduced into F by small pipettes with turned-up ends, any air simultaneously introduced being sucked out. The gas is then passed over from A to F, shaken with the absorbent and returned; the spent absorbent is then removed. The explosion analysis is carried out in the explosion tube E, which is provided with a mercury reservoir H.

The absorbents used are somewhat different, as they are used in contact with mercury.

They are :—

(1) *Caustic Potash :* 1 lb. in 500 c.c. water.

(2) *Pyrogallol :* 1 oz. in 100 c.c. water (no alkali is added).

(3) *Bromine :* 10 per cent. of potassium bromide is added to saturated bromine-water.

(4) *Ammoniacal Cuprous Chloride :* 50–75 grammes of cuprous chloride are suspended in 250 c.c. of water containing 10 to 15 grammes of ammonium chloride, and 0·880 ammonia added till no more dissolves and the solution smells distinctly of ammonia. Five grammes more cuprous chloride are then added; in a few hours the smell of ammonia should disappear.

The inner surfaces of A and B are kept moist with dilute

sulphuric acid (1 : 20). In measuring the gas the mercury is drawn over to a pre-determined mark on the capillary tubing above A. The pressure readings are obviously independent of the atmospheric pressure. Temperature changes are allowed for by taking the temperature of the running-water-jacket surrounding A and B. A small telescope is used to facilitate the readings. A "vacuum" reading with no gas in A should first be taken.

C.c. 5–8 of potash are used to absorb the carbon-dioxide. The residual gas is measured and 2 c.c. of pyrogallol are then added to the potash and the gas passed back, oxygen thus being absorbed. The spent alkaline pyrogallol is then rejected.

The ethylene, etc., is then absorbed by bromine, and the carbon-monoxide by cuprous chloride. In each case the gas is freed from acid or ammoniacal fumes by means of potash or dilute acid before measurement. Two successive portions of 8 to 10 c.c. of cuprous chloride are required to remove carbon-monoxide.

The explosion analysis is made by the help of oxygen, stored in a small gas holder over glycerine-water (equal parts). If nitrogen is only determined by difference the oxygen need not be absolutely pure. The volume of excess oxygen required is double that of the "knall-gas" obtained by adding the theoretical amount of oxygen for complete combustion. Electrolytic gas may be added if required to render the mixture explosive.

MINE AIR

For this purpose Haldane's apparatus (Fig. 15) may be used, and can be obtained in portable forms. For laboratory use the apparatus consists of a bulbed measuring tube A (the bulb holding 15 c.c. and the stem 7 c.c.), which is connected with the levelling tube B, containing mercury. A compensating tube N is provided, and the pressures in A and N are adjusted to equality by using the potash absorption pipette E as a manometer, the potash being

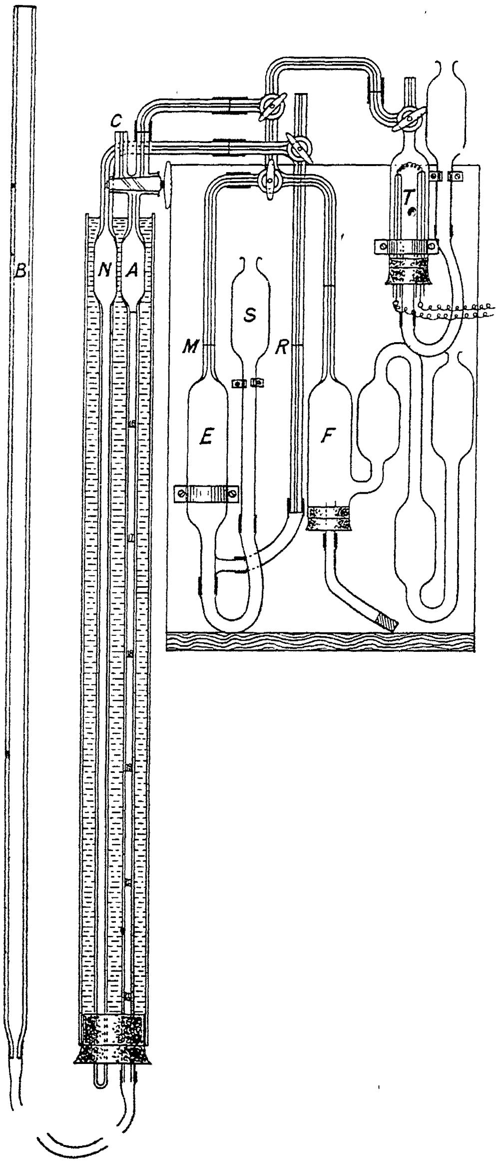

FIG. 15.—HALDANE'S APPARATUS FOR ANALYSIS OF MINE AIR.

adjusted to the marks M and R by manipulating B and S. A fine adjustment of the height of B can be made by a rack-

and-pinion. A and N are water-jacketed. Before making an analysis the connecting tubes are swept out with nitrogen (left from the previous analysis or else prepared by absorbing the oxygen from ordinary air). The gas is drawn in at C, and measured after adjusting the pressure as described. Carbon-dioxide is then absorbed by passing the gas in and out of E a few times, after which the volume is again read. Methane is then burnt in the combustion pipette T by means of an electrically heated platinum spiral, care being taken not to overheat the spiral at first. The gas after cooling is remeasured. The carbon-dioxide formed is then absorbed and is equal to the volume of methane present; the contraction should be twice this volume. A second combustion should be made to ensure the completeness of the action, as a little gas in the air-space of the potash pipette otherwise escapes combustion.

The remaining oxygen is then estimated by absorption in the pyrogallol pipette F, care being taken to rinse out the gas in the dead-space of the potash bulb by passing the gas into it after the absorption is complete, and then back into the pyrogallol pipette. To the oxygen so found must be added that used in burning the methane, which is twice the volume of the methane.

ETHANE

"Straight" coal gas may be expected to contain ethane, which is undoubtedly formed by the low-temperature distillation of coal, because, although this is admittedly unstable at high temperatures it is nevertheless more stable under such conditions than ethylene, which is invariably present in coal-gas. Nevertheless the presence of ethane in coal-gas is usually ignored because a mixture of equal volumes of hydrogen and ethane behaves on combustion exactly like a similar volume of methane :—

$$\begin{array}{lll} 2CH_4 + 4O_2 & = & 2CO_2 + 4H_2O. \\ \text{2 vols. 4 vols.} & & \text{2 vols. (4 vols.)} \\ \underbrace{H_2 + C_2H_6}_{\text{2 vols.}} + 4O_2 & = & 2CO_2 + 4H_2O. \\ \quad\quad\quad\quad\quad\quad\text{4 vols.} & & \text{2 vols. (4 vols.)} \end{array}$$

Unless therefore there were more ethane present than hydrogen (a case never met with), it would be impossible by the combustion method to obtain even a qualitative indication of the presence of ethane *unless the hydrogen is separately estimated.* Any ethane present will simply be estimated, together with its own volume of hydrogen, as methane, and this will not affect the accuracy of the determination of the residual nitrogen by difference. Note that the calorific value of methane is very nearly the mean of the calorific values of hydrogen and ethane, so that disregard of the presence of ethane will not affect the calculation of the calorific value of coal gas from its analysis.

MINOR CONSTITUENTS OF COAL GAS

The method consists in passing a large volume of the gas, measured by means of a gas-meter, through a train of absorption vessels in which the constituent to be determined is absorbed, and afterwards estimated gravimetrically or volumetrically. The gas-meter readings must be reduced to 15° C. and 760 mm. as described under Gas Calorimetry.

For most purposes the gas should be passed at a rate of two-thirds of a cubic foot per hour, unless specially efficient absorption apparatus is available. Crude gas should first be filtered through a cotton-wool plug.

AMMONIA [1]

Short test: 10 cubic feet of gas are passed through an absorption vessel containing 50 c.c. of $\frac{N}{10}$ acid; the Gas Referees' tube, packed with glass beads, is suitable. The acid is rinsed out into a beaker and the excess titrated with $\frac{N}{10}$ soda. The acid corresponding to the ammonia is given by difference.

Long test: 100 cubic feet of gas are passed through a

[1] The volumes of gas stated apply to purified gas, and can be much reduced when testing crude gas.

wash bottle containing 10 per cent. sulphuric acid. The ammonia is afterwards estimated by distillation.

BENZOL

Short test: 10 cubic feet of gas are passed through :—

(1) A large U-tube containing calcium chloride.

(2) A weighed "potash bulb," containing creosote oil, distilled up to 200° C., provided with an exit calcium chloride tube. The increase in weight of this bulb gives the weight of benzol.

Long test: 100 cubic feet of gas are passed through a series of three wash-bottles of creosote oil distilled up to 200° C. The benzol absorbed is recovered by redistilling the oil up to 200° C., and measured. If enough is obtained it may be further examined as already described.

The estimation of benzol may be combined with that of ammonia, the former being first absorbed. If the gas pressure is insufficient to overcome the back pressure of the absorption apparatus, a filter pump must be used to draw the gas through.

See also Rhead, *J.S.C.I.* 1917, **36**, 768; also *Gas Journal*, February 11, 1919, for Paris Gas Works freezing method.

NAPHTHALENE

Ten cubic feet of gas are passed first through a wash-bottle containing oxalic or citric acid solution, to remove ammonia, and then through three wash-bottles which contain 150 c.c. of saturated picric acid solution (accurately measured); at the conclusion of the test the contents of the second and third bottles are drained into the first, which is then exhausted of air by a filter pump, with the help of a cork, and tube sealed at one end, but having a lateral opening, as previously described in the Estimation of Naphthalene from Coal Tar (page 66).

The exhausted bottle is heated for two hours in a water bath and allowed to stand overnight. The liquid is then filtered through a dry filter (the precipitate not being washed)

and 100 c.c. of the filtrate are titrated with $\frac{N}{10}$ caustic soda solution, using lacmoid (in considerable amount) as indicator. C.c. 100 of the original picric acid $\left(\text{which is about } \frac{N}{20}\right)$ are also titrated. Difference gives the $\frac{N}{10}$ soda equivalent to the picric acid which has united with the naphthalene; it must be multiplied by 1·5 to allow for the 50 c.c. discarded. (1 c.c. $\frac{N}{10}$ solution = 0·0128 grammes naphthalene).

CARBON DIOXIDE

This may be absorbed by a weighed potash bulb provided with a calcium chloride tube. To get an accurate result the gas must first be freed from :—

(1) Sulphuretted hydrogen, by a U-tube containing bog iron ore.

(2) Benzol, by a U-tube containing pumice soaked in creosote oil.

(3) Moisture, by a U-tube containing calcium chloride (previously saturated with carbon dioxide).

HYDROCYANIC ACID

A hundred cubic feet of gas are passed first through a U-tube containing lead carbonate, which removes any sulphuretted hydrogen present, and then through absorption bulbs containing 100 c.c. of $\frac{N}{100}$ iodine solution, and a little $NaHCO_3$ and coloured blue by the addition of starch solution; the blue colour should remain throughout the passage of the gas. The excess of iodine remaining at the close of the experiment is titrated with $\frac{N}{100}$ thiosulphate solution, and the iodine equivalent of the hydrocyanic acid found by difference (1 c.c. $\frac{N}{100}$ iodine = 0·000135 grammes HCN). Alternatively the hydrocyanic acid may

be absorbed in 10 per cent. caustic soda solution containing a little potassium iodide, the solution being afterwards titrated with $\frac{N}{100}$ silver nitrate solution until a permanent turbidity is obtained. (1 c.c. $\frac{N}{100}$ silver nitrate = 0·00054 grammes HCN).

SULPHURETTED HYDROGEN

A hundred cubic feet of gas are passed through ammoniacal zinc chloride solution, and the precipitated sulphide is well washed with warm water and washed into 25 c.c. of $\frac{N}{10}$ iodine solution. This solution is then acidified with cold dilute hydrochloric acid and well shaken; when the precipitate has dissolved the excess of iodine is titrated with $\frac{N}{10}$ thiosulphate solution. (1 c.c. $\frac{N}{10}$ iodine = 0·0017 grammes H_2S).

TOTAL SULPHUR

For this test the Referees' method is invariably adopted. The gas is burnt under a glass "trumpet tube" in a Bunsen burner with a steatite top, mounted on a perforated metal stand, on which about 2 oz. of commercial ammonium carbonate are placed. The sulphur dioxide formed by the combustion reacts with the ammonia fumes and condenses with the water which is also formed, in a tower packed with glass marbles, the liquid dripping from a small glass tube penetrating the base of the tower into a beaker. The other gases pass from the tower into a long inclined glass condenser, which creates the necessary draught. Ten cubic feet of gas are burnt at the rate of two-thirds of a cubic foot per hour, the meter being arranged to cut off the gas automatically when this quantity has passed. It is advisable to rinse the tower with strong ammonium carbonate solution before starting the test.

At the end of the test the chimney and tower are rinsed

into the beaker with distilled water and the contents of the beaker are then treated with bromine water and hydrochloric acid, well boiled, and precipitated as usual with barium

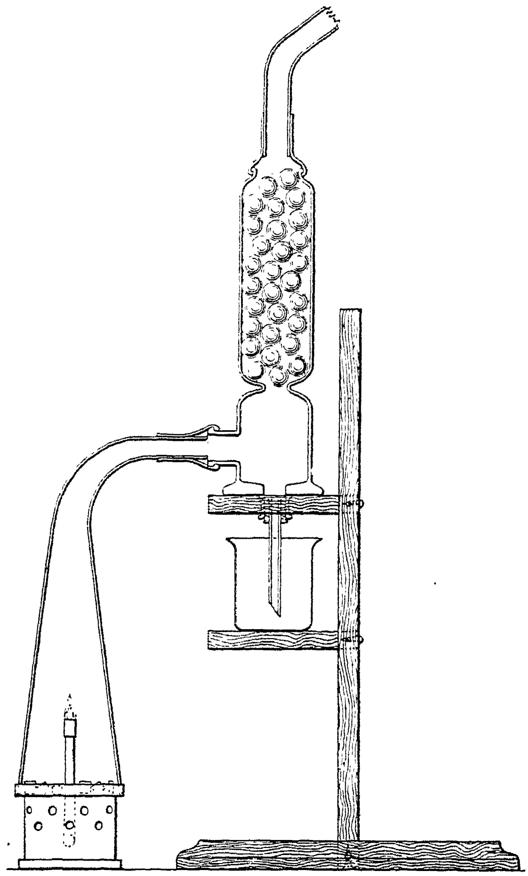

FIG. 16.—GAS REFEREES' SULPHUR TEST.

chloride solution (1 gramme $BaSO_4$ = 0·1373 gramme S).

Note.—1 gramme = 15·432 grains; by the use of this relationship all the foregoing results may be readily expressed as grains per 100 cubic feet.

CHAPTER X

CALORIMETRY AND PYROMETRY

BOMB CALORIMETER

THIS is an instrument for the combustion of solid or liquid fuels in oxygen at 25 atmospheres pressure (FIG. 17). It consists of a closed bomb lined with porcelain (gold or platinum) having a cover screwed on gas-tight by means of a lead washer. Through the cover passes :—

(1) A screw-valve to admit oxygen and to allow it to escape after the determination.

(2) A terminal insulated by a porcelain collar, to allow of electrical ignition of the charge.

Two stout wires, one connected to the terminal and the other to the metal of the cover, reach to about the centre of the bomb, and one of them carries a horizontal loop which serves to support the platinum or porcelain capsule in which the charge is placed. In the case of coal this would consist of about a gramme of powdered coal, compressed into a pellet; for oils about 0·6 gramme, absorbed in kieselguhr, would be used. The two wires are bridged across by a fine platinum or iron wire which touches the fuel. This wire is electrically fused by a current of two ampères at twelve volts when it is desired to ignite the fuel. The soundness of the connections may be tested at any stage by the momentary application of four volts, when a spark should be obtained on breaking the circuit.

The bomb is filled with oxygen from a cylinder with the help of an auxiliary valve and manometer; the pressure should rise very gradually. It is then placed in the calorimeter, which holds a known weight (about $2\frac{1}{2}$ litres) of water and is surrounded by a water-jacket, an air-space

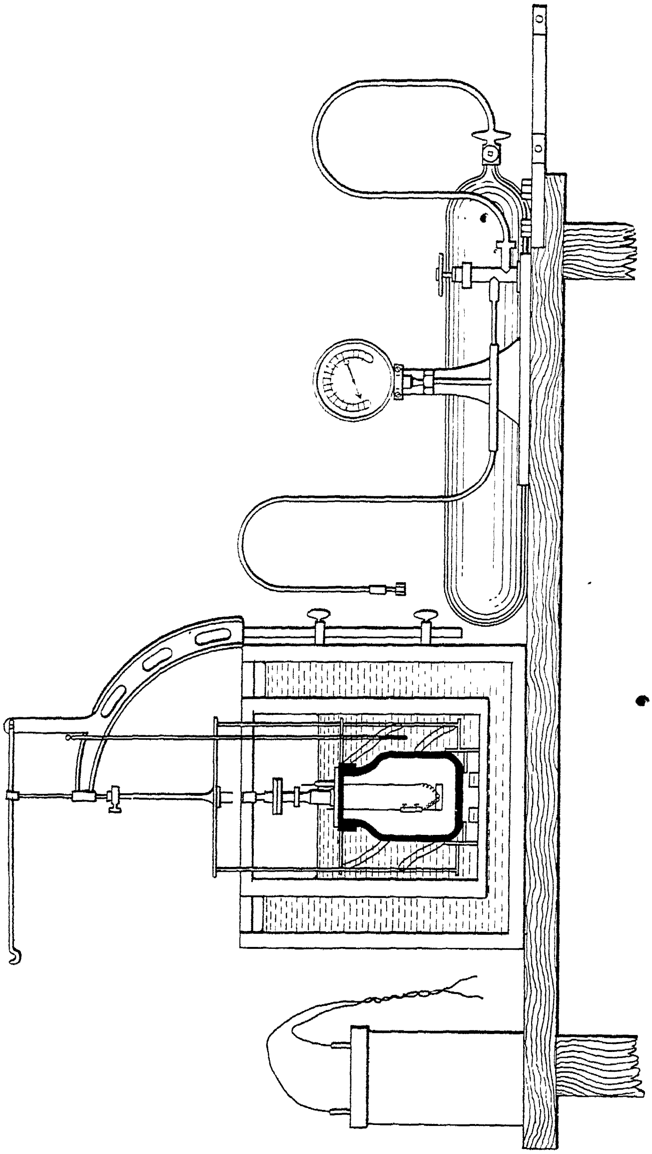

FIG. 17.—MAHLER-COOK BOMB CALORIMETER.

intervening. All the water used should be at the temperature of the laboratory. The water in the calorimeter is stirred by a set of paddles operated by hand or electrically,

its temperature is read by a delicate thermometer reading easily to hundredths of a degree Centigrade.

After stirring for a little while, temperature observations are begun, and continued at minute intervals. At the end of the fifth minute the charge is fired. Further readings are taken at $5\frac{1}{2}$, 6, 7 . . . minutes until the temperature reaches a maximum, and then for five minutes longer. The rise in temperature is obtained by subtracting the temperature at ignition from the maximum, and is corrected by adding an amount representing the heat lost by the bomb in reaching the maximum. The rate of loss may be assumed to be :—

(1) From 5 to $5\frac{1}{2}$ minutes, as in the initial period.

(2) From the maximum back to such time that the temperature is one degree lower, as in the final period.

(3) For the rest of the time, as in the final period minus 0·005° C. per minute.

The following example (Mahler) shows the details of the calculation :—

Initial Period :—

0 mins.	10·23°C.
1 ,,	10·23
2 ,,	10·24
3 ,,	10·24
4 ,,	10.25
5 ,,	10·25

$$\text{Rise} = \frac{10{\cdot}25 - 10{\cdot}23}{5} = 0{\cdot}004^\circ \text{ C. per min.}$$

Period of Combustion :—

5 mins.	10·25° C.	Gain $= \frac{1}{2} \times 0{\cdot}004 = 0{\cdot}002^\circ$ C.
$5\frac{1}{2}$,,	10·80	
6 ,,	12·90	Loss $= \frac{1}{2} \times (0{\cdot}012 - 0{\cdot}005) = 0{\cdot}0035^\circ$ C.
7 ,,	13·79	Loss $= 2 \times 0{\cdot}012 = 0{\cdot}024^\circ$ C.
8 ,,	13·84	

$$\text{Nett Loss} = 0{\cdot}024 + 0{\cdot}0035 - 0{\cdot}002 = 0{\cdot}0255^\circ \text{ C.}$$

Final Period :—

8	mins.	13·84°C.	Fall $= \dfrac{13{\cdot}84 - 13{\cdot}78}{5} = 0{\cdot}012°$ C. per min.
9	,,	13·82	
10	,,	13·81	
11	,,	13·80	
12	,,	13·79	
13	,,	13·78	

Hence we have $\begin{cases} \text{uncorrected rise} = 13{\cdot}84 - 10{\cdot}25 = 3{\cdot}59° \text{ C.} \\ \text{corrected rise} = 3{\cdot}59 + 0{\cdot}0255 = 3{\cdot}6155° \text{ C.} \end{cases}$

If T is the corrected rise in temperature (°C.) and W the total weight of water used (grammes), T × W gives the number of calories given out by the known weight in grammes of coal on burning, and $\frac{9}{5}$ T.W gives the corresponding number of B.Th.U. per lb.

The total weight of water, W, includes the water equivalent of the calorimeter. This is best determined once for all by the use of a substance of known calorific value, such as :—

Benzoic acid . .	6333	cals. per gramme.
Cane sugar . . .	3956	,, ,, ,,
Naphthalene . .	9664	,, ,, ,,

The following minor corrections may be noted, though they are seldom required in practice :—

(1) Electrical ignition : − 0·24 cals. per volt-ampère-second.

(2) Oxidation of iron wire, if used : − 1·6 cals. per milligramme.

(3) Unburnt carbon (*e.g.* in fused ash) : + 8·1 cals. per milligramme.

(4) Formation of nitric and sulphuric acids, which does not occur at atmospheric pressure (the total acid is titrated, and the sulphuric acid precipitated by barium chloride—an excellent method for determining sulphur in fuels). The correction is 230 cals. per gramme of HNO_3 formed, plus 730 cals. per gramme of H_2SO_4 formed.

N.B.—The bomb should contain a little water to absorb these acids, which water must of course be added to its "water equivalent."

(5) *Correction to constant pressure.*—In the bomb combustion occurs at constant volume, hence the thermal effect of the contraction (due chiefly to condensation of water) which occurs on combustion at constant (atmospheric) pressure is not obtained. For 1 gramme of fuel the correction is + 1·44 calories per 1 per cent. of "unoxidised hydrogen" $\left(H - \frac{O}{8}\right)$. For an oil of the composition C_7H_{16} (molecular weight = 100) this would amount to $16 \times 1{\cdot}44 = 23$ calories.

(6) *Correction for specific heat of water.*—If the mean temperature is not 15° C., the specific heat of water will not be exactly unity, the value being 1·0016 at 10° C. and 0·9989 at 20° C.

The calorific value of coal may be approximately calculated from its composition by the formula

$$\frac{1}{100}\left(8137\,C + 34500\left(H - \frac{O}{8}\right) + 2220\,S\right)$$

where C, H, O, S are the percentages of these elements present.

GAS CALORIMETRY

All the instruments in use are very similar in principle; the description following refers especially to the Simmance-Abady Calorimeter (FIG. 18).

The method consists in burning the gas (measured by a wet gas-meter which must be carefully filled up to the water-line) at a constant rate (5 cubic ft. per hour) in a Bunsen burner, adjusted so as to be just non-luminous; the flame is about 7 in. long and should be adjusted before placing it in the calorimeter. Fluctuations of gas pressure must be eliminated by the use of a governor, which should be placed after the gas-meter. If the governor is hanging freely, a very slight touch should alter the flame; if neces-

sary the weight may be adjusted by a slip of lead placed as a rider on the balance arm. The governor is filled with water[1] up to the plug line. On closing its outlet tap the gas-meter reading should remain constant if there is no leak.

The hot flame-gases are cooled by contact with pipes through which a steady stream of water flows from a constant level about 10 ft. high. A ball valve cistern may be used. The rate of flow is from 1,800 to 2,000 c.c. per minute, during which time the gas-meter hand makes one revolution ($\frac{1}{12}$ cubic ft.). The temperature of the water entering and leaving the calorimeter is taken by two thermometers graduated in tenths of a degree Centigrade, arranged side by side; with the above arrangements the difference will be about 7° C. The temperature of the escaping gases is taken by a third thermometer and should not be more than 2° C. greater than the inlet water thermometer reading. A small damper is provided for regulating the escape of these gases, and their temperature may be controlled to some extent by partially closing it. The steadiness of the water flow is gauged by the constancy of the water-level in an open glass tube inserted just before the water exit; the water line should be about half-way up the tube.

Before starting the calorimeter, air is displaced from the water circuit by a rapid current of water, the level tube being plugged. Before making a test the calorimeter should have been running steadily for some time. Each test occupies 1 gas-meter revolution, during which time the water is collected in a graduated cylinder (a change-over funnel being provided). Four or five pairs of readings of the thermometers are taken during this time, and the mean temperature difference calculated; this, multiplied by the weight of water collected, gives the number of calories generated by the combustion of $\frac{1}{12}$ cubic ft. of gas. Hence the number of calories per cubic ft. is easily calculated, and 3·97 times this

[1] Dilute dichromate solution may be used instead of water, to avoid rusting of the governor.

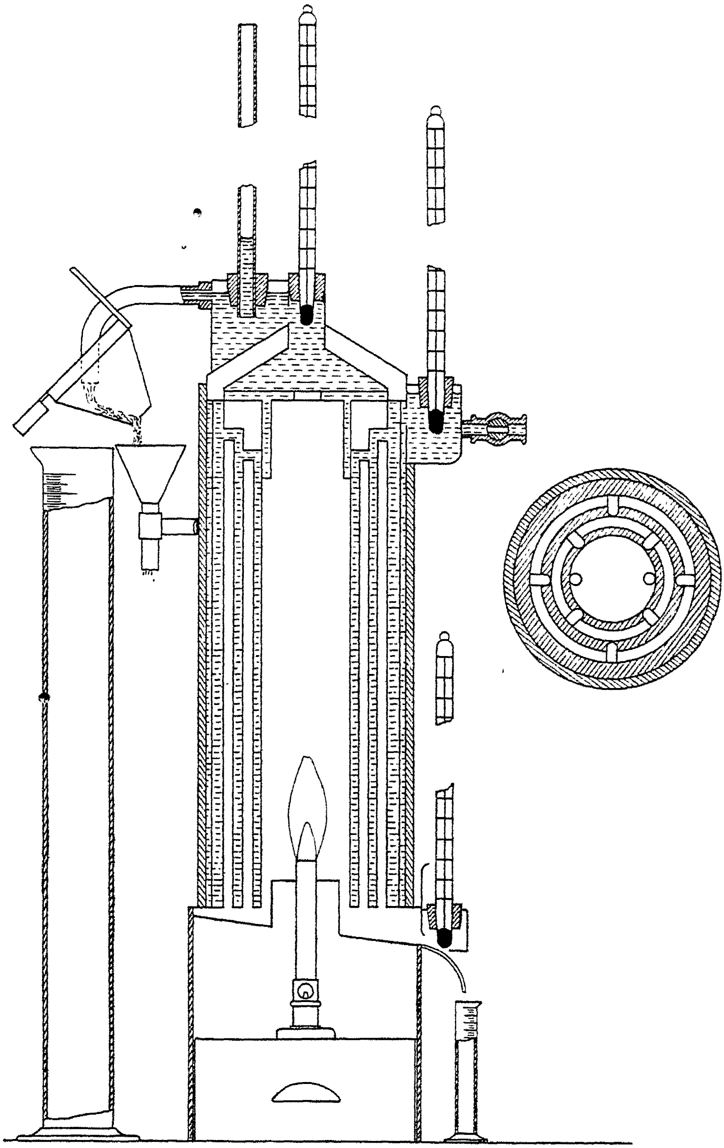

FIG. 18.—SIMMANCE-ABADY GAS CALORIMETER.

figure gives number of B.Th.U. A table to facilitate this calculation is given in the APPENDIX.

The following precautions should be noted :—

(1) The inlet and outlet thermometers must be very carefully compared side by side in a water bath at constant temperature; any difference found must be subtracted from (or added to) the rise in temperature during the experiment.

(2) The mean of several successive results is required.

Further, in measuring the water collected, its temperature should also be noted so that its density and hence its weight may be found. The temperature of the gas in the meter (by the thermometer provided) and the difference of its pressure from the observed atmospheric pressure at the time of the experiment (by a small water manometer attached to the run-off tap of the meter) should also be noted in order to reduce the volume of gas burnt to 15° C. and 760 mm. (wet) the usual standard.

Radiation is reduced by lagging the calorimeter with wood, and by arranging that the water flowing through it acts as a jacket before contact with the hot gases. The correction for radiation is very small (under 1 per cent.), and also difficult to estimate, hence it is invariably neglected.

It is best to use water of the same (initial) temperature as the air of the laboratory.

As, in practice, the water formed by the combustion of gases does not condense, it is usual to calculate, besides the above "gross" calorific value, a "nett" calorific value. The water from the combustion of a known volume of gas in the calorimeter is collected as it drips out of the condensed water outlet and accurately measured or weighed; 600 calories are deducted from the "gross" calorific value for every gramme of water condensed per cubic foot of gas burnt—this being the latent heat of evaporation of water at the ordinary temperature. For solid and liquid fuels the "nett" value differs very little from the "gross" value.

Before starting the calorimeter water should be poured in the gas outlet till it drips from the condensed water outlet, and the calorimeter should run at least two hours before

attempting to collect the water condensed, otherwise the flow of condensed water will be found to be most erratic. It is advisable to collect a fairly large quantity of water, and this presents no difficulty, as the calorimeter will look after itself during the process and need not be adjusted as carefully as during the actual test; all that is required are the initial and final gas-meter readings.

The gas burnt and the products of combustion are both saturated with water-vapour, while the air for the combustion (usually) is not, so that a little moisture that would otherwise condense does not and so makes the gross calorific value too low. (If the air for combustion is almost saturated the correction may possibly be negative, as there is a slight contraction on combustion, so that the ingoing moisture may be more than sufficient to saturate the burnt gases.)

The gas Referees (using Boys' calorimeter) introduce an approximate correction for this, namely $0{\cdot}15\ [6{\cdot}6c - (7a + b)]$ B.Th.U. per cubic foot. Here a, b and c are the number of grains of water in a cubic foot of air, gas and effluent gases respectively, found by the help of a wet and dry bulb hygrometer in the case of the air, and by the ordinary thermometer readings in the case of the (saturated) gas and products of combustion. (*See* Glaisher's, or similar, tables.) The formula assumes that 1 volume of gas is burnt with 7 volumes of air (about 50 per cent. in excess of the theoretical amount) to give 6·6 volumes of burnt gases after condensation of the water; it therefore only holds for coal gases of average composition, but may readily be modified to suit special cases. The effluent gases are usually a little above air temperature, but if the water circulated is rather cold, they may fall below it, the apparent calorific value being diminished in the first case and increased in the second. The approximate correction for this effect, on the above assumptions, is $+\ 0{\cdot}00022\ de$, where d is the weight in grains of a cubic foot of air saturated at the temperature of the effluent gases (from Glaisher's tables) and

e is the difference between this temperature and the air temperature.

These corrections[1] are only introduced where great accuracy is required, or where the conditions are somewhat abnormal (*e.g.* the escaping gases hotter than usual; in this case, however, the test would be repeated if possible).

As a check, the calorific value of the gas may be calculated from its analysis: the difficulty lies in the fact that this is not quite complete. In particular, "unsaturated hydrocarbons" include, besides ethylene with up to 30 per cent. of propylene, smaller quantities of benzene and naphthalene, etc., of very high calorific value. By comparing "observed" and "calculated" results in a large number of cases we have concluded that the amount of these latter substances in "straight" coal gas, "stripped" of most of its benzol, is fairly constant whatever the total quantity of "unsaturated hydrocarbons," doubtless owing to the saturation of the gas with these vapours. Accordingly, to make the figures tally, the calorific value assumed for the "unsaturated hydrocarbons" must be lower the higher the percentage of these.

We recommend provisionally the following values:—

Unsaturated Hydrocarbons. Per cent.	Gross Calorific Value (B.Th.U. per c. ft. at N.T.P.).
2	4,200
2·5	3,900
3	3,500
3·5	3,200
4	2,800

For the other combustible gases the values are (in the same units):—

	Gross.	Nett.
H_2	343·3	287·2
CO	341·4	341·4
CH_4	1064·0	951·3

[1] In any case the *nett* value must be calculated from the uncorrected gross value: the correction is automatically made by the small variation in the amount of condensed water collected

To reduce the value calculated for the dry gas at N.T.P. to that for the wet gas at 15° C. and 760 mm. pressure, multiply by 0·932.

RECORDING CALORIMETER

Simmance has recently modified the calorimeter just described to give a continuous record. Beside the inlet and outlet thermometers are placed two air thermometer bulbs communicating by narrow pipes with two cylindrical pressure-drums, which are corrugated parallel to their plane faces so as to expand or contract axially with changes of internal pressure. These, acting in opposition along their common axis, move the short arm of a lever backwards or forwards according to the prevailing temperature difference in the calorimeter, to which the calorific value is proportional, the rate of burning the gas and of the water-flow being kept constant. The long arm of the lever carries a pen which records the calorific value on an empirically graduated chart without the intervention of any gearing. The instrument is set by doing a determination in the usual way. Other determinations can be done whenever desired without interrupting the record, it being merely necessary to put the gas-meter in circuit by turning a few taps. In addition to the ordinary balance type of governor, this calorimeter is provided with a second very sensitive governor which acts as a fine adjustment of the gas-pressure. The whole of the recording apparatus is separately housed in a glass case, through the length of which the chart stretches, being wound on rollers at the top and bottom and thus completely visible.

PYROMETRY may be defined as the art of measuring high temperatures. Below are described three accurate and convenient pyrometers.

THE THERMO-COUPLE

This depends on the fact that an electric current flows round a circuit of two dissimilar wires if the junctions are

at unequal temperatures. A galvanometer placed in the circuit is affected by this current, and its scale can be graduated to give the temperature-difference directly; alternatively, if the "cold junction" is maintained at a constant temperature, the scale may give the temperature of the "hot junction" directly.

The use of metals for this purpose is restricted to those which can withstand the temperature to be measured, and at the same time give an electromotive force increasing regularly with the temperature.

A couple with one wire of pure platinum and the other of the same metal alloyed with 10 per cent. of rhodium is very satisfactory for regular use up to 1000° C., and for occasional readings up to 1400° C. Owing to the expense, cheaper substitutes have been found, which are however less durable and for the most part fail at lower temperatures. The wires must, of course, be insulated (usually by threading through fireclay tubing) except just at the hot junction where they are welded together; they must further be protected by enclosure in a refractory tube. The thermo-couple may easily be adapted to give a continuous record.

The calibration of a thermo-couple is very easily effected by using it to determine the melting or boiling points of pure substances which have been accurately found by the use of a gas thermometer. Convenient substances are :—

Tin (melting point)	231·9° C.	Water (boiling point)	100·00° C.
Cadmium ,,	321·0	Naphthalene ,,	218·0
Zinc ,,	419·4	Benzophenone ,,	306·0
Aluminium ,,	657	Sulphur ,,	444·7
Common Salt ,,	801		
Potassium Sulphate ,,	1070		

Boiling points may be found by Barus' apparatus, which consists of a glass tube 30 cm. long and 1·5 cm. in diameter, closed at one end. It is surrounded for 15 cm. with a cylindrical "muff" of plaster of paris, 10 cm. in diameter, through which the closed end projects for 7 cm. Near the

open end, just above the muff, a bulb is blown, which prevents the tube from slipping through the muff. The substance used should fill the tube to a depth of 4·5 to 5 cm.; it is boiled over a Bunsen flame so that the line of condensation of the vapour is mid-way up the bulb. The thermo-junction is then placed within the jacketed part of the tube, and the temperature observed.

To determine a melting point the material is melted in a suitable crucible and withdrawn from the furnace. The thermo-couple (in its protecting tube) is quickly fixed vertically with the hot-junction dipping well into the liquid[1] and temperature observations are taken every few minutes. When the melting point is reached the temperature will remain practically stationary until the whole of the substance solidifies.

If the reading of the thermo-couple does not then agree with the figures given above, a correction should be made when using the instrument at this temperature. By plotting the corrections against the (apparent) temperatures a curve is obtained by which the correction to be applied at any given temperature may be found.

A thermo-couple calibrated in this way may be used to check the lower readings of the pyrometers next to be described.

FÉRY'S RADIATION PYROMETER

This instrument (FIG. 19) actually measures the heating effect of the radiant energy from a hot body, and the corresponding temperature can be deduced in the special case of a "black" body (*i.e.* one which absorbs all radiant energy incident on it). Glowing coke, copper oxide and other black metallic oxides approach very nearly to this condition, while on the other hand metals like platinum show a considerable divergence from it.

Fortunately an enclosed space, of whatever material

[1] The hot junction should previously be heated in the furnace, so that it quickly assumes the temperature of the molten material.

composed, if maintained at a uniform temperature, behaves in an exactly equivalent manner to a black body because any energy reflected from one part of its surface strikes the surface again elsewhere, and so is eventually completely absorbed. The method can accordingly be applied to take the temperature of enclosed furnaces of uniform tempera-

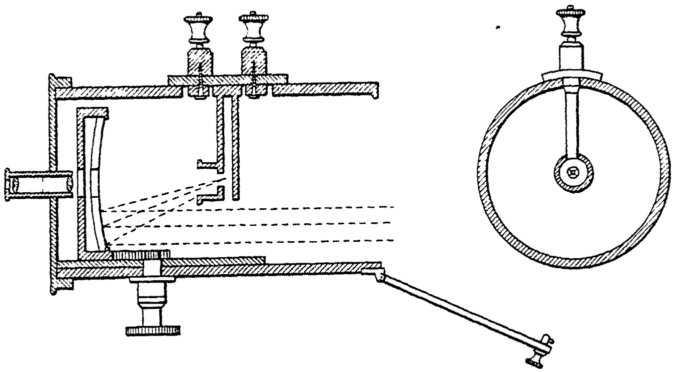

FIG. 19.—FÉRY RADIATION PYROMETER.

ture through a small sight-hole. A further extension is readily possible by use of a closed tube inserted in a furnace of any sort, the radiation from the closed end being examined through the open end.

According to Stefan and Boltzmann's law, the total energy radiated from a black body varies as the fourth power of the absolute temperature.

In Féry's instrument the radiation from the sight hole is focussed by means of a concave mirror on to a small thermo-junction which is connected to a delicate galvanometer, graduated to give the furnace-temperature directly. So long as the image of the hole does not overlap the thermo-junction the distance of the pyrometer from the furnace does not matter. The focussing is done by observation through a hole in the centre of the concave mirror, an optical device showing the sight hole, when out of focus, as a divided circle with its halves laterally displaced about the horizontal diameter.

The instrument being entirely external to the hot body does not deteriorate and can be used up to the highest attainable temperatures assuming the validity of Stefan's law at these temperatures. Its readings, however, are affected by the slow heating of the air inside the instrument which causes the indicator to "creep." If this occurs the instrument must then be allowed to cool before further use.

Instead of a thermo-couple any delicate thermometer might be used. In a modified instrument Féry employs a spiral spring of two metals, the unequal expansion of which uncoils the spring and works the pointer showing the temperature.

WANNER'S OPTICAL PYROMETER

It is a familiar fact that the intensity of the light from a hot body increases with the temperature. As quantitative measurements involve the use of some photometric device of which the observer's eye is an essential part, it is evident that instruments of this class cannot be made self-recording. As the colour of the light changes with the temperature, the measurement has to be restricted to light of a definite colour. Under such conditions the relation between the intensity I and the absolute temperature T is given in the case of a "black" body by Wien's law, *viz.* :—

$$\log\ I = a - \frac{b}{T} \quad \text{where } a \text{ and } b \text{ are constants.}$$

It should be added that optical pyrometers are less affected by departure from "black body" conditions than radiation pyrometers.

In Wanner's pyrometer the light from the furnace is compared with that of a small 4 volt electric lamp. Entering the instrument through parallel slits the beams are rendered monochromatic by passage through a prism and screen arranged to isolate a narrow band in the red; they are then oppositely polarised and observed through an eyepiece containing an analyser, by rotating which the relative

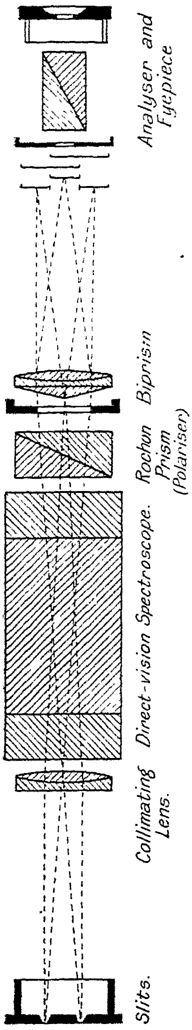

FIG. 20.—WANNER OPTICAL PYROMETER.

amounts of the two rays transmitted can be varied in any desired ratio. The analyser is adjusted so that the two halves of the field appear equally bright, when the temperature is read off on the attached scale.

The instrument is set by sighting it on the flame of a Hefner Amyl-Acetate lamp placed in a definite position with respect to it. It should then read 1400° C., and if it does not the current through the comparison lamp must be adjusted by a rheostat until the desired reading is obtained. If this current is measured by a milliammeter and kept constant at this value, the pyrometer need not be reset as long as the circuit is not changed.

The pyrometer may also be set by sighting on a body of known temperature.

Wanner's pyrometer cannot be used below 900° C., owing to the amount of light absorbed by the optical arrangements.

In other instruments of this class the prism is replaced by red glass and the polarising arrangements by adjustable diaphragms, or screens of smoked glass. These can be used at lower temperatures.

APPENDIX

1920

INTERNATIONAL ATOMIC WEIGHTS

	Symbol.	Atomic Weight.		Symbol.	Atomic Weight.
Aluminium	Al	27·1	Neodymium	Nd	144·3
Antimony	Sb	120·2	Neon	Ne	20·2
Argon	A	39·9	Nickel	Ni	58·68
Arsenic	As	74·96	Niton (radium emanation)	Nt	222·4
Barium	Ba	137·37	Nitrogen	N	14·008
Bismuth	Bi	208·0	Osmium	Os	190·9
Boron	B	10·9	Oxygen	O	16·00
Bromine	Br	79·92	Palladium	Pd	106·7
Cadmium	Cd	112·40	Phosphorus	P	31·04
Cæsium	Cs	132·81	Platinum	Pt	195·2
Calcium	Ca	40·07	Potassium	K	39·10
Carbon	C	12·00	Praseodymium	Pr	140·9
Cerium	Ce	140·25	Radium	Ra	226·0
Chlorine	Cl	35·46	Rhodium	Rh	102·9
Chromium	Cr	52·0	Rubidium	Rb	85·45
Cobalt	Co	58·97	Ruthenium	Ru	101·7
Columbium	Cb	93·1	Samarium	Sa	150·4
Copper	Cu	63·57	Scandium	Sc	44·1
Dysprosium	Dy	162·5	Selenium	Se	79·2
Erbium	Er	167·7	Silicon	Si	28·3
Europium	Eu	152·0	Silver	Ag	107·88
Fluorine	F	19·0	Sodium	Na	23·00
Gadolinium	Gd	157·3	Strontium	Sr	87·63
Gallium	Ga	70·1	Sulphur	S	32·06
Germanium	Ge	72·5	Tantalum	Ta	181·5
Glucinum	Gl	9·1	Tellurium	Te	127·5
Gold	Au	197·2	Terbium	Tb	159·2
Helium	He	4·00	Thallium	Tl	204·0
Holmium	Ho	163·5	Thorium	Th	232·15
Hydrogen	H	1·008	Thulium	Tm	168·5
Indium	In	114·8	Tin	Sn	118·7
Iodine	I	126·92	Titanium	Ti	48·1
Iridium	Ir	193·1	Tungsten	W	184·0
Iron	Fe	55·84	Uranium	U	238·2
Krypton	Kr	82·92	Vanadium	V	51·0
Lanthanum	La	139·0	Xenon	Xe	130·2
Lead	Pb	207·20	Ytterbium (Neoytterbium)	Yb	173·5
Lithium	Li	6·94	Yttrium	Yt	89·33
Lutecium	Lu	175·0	Zinc	Zn	65·37
Magnesium	Mg	24·32	Zirconium	Zr	90·6
Manganese	Mn	54·93			
Mercury	Hg	200·6			
Molybdenum	Mo	96·0			

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

LOGARITHMS (*continued*)

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9328	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

ANTILOGARITHMS (*continued*)

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	16	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

DENSITY OF HYDROCHLORIC ACID, $HCl . Aq$

Grammes per c.c. at 15° C. (Lunge and Marchlewski, 1891.)

Dens.	Grammes HCl in 100 gm. of Solution.	Grammes HCl in 1 litre of Solution.	Dens. Change for ± 1°.	Dens.	Grammes HCl in 100 gm. of Solution.	Grammes HCl in 1 litre of Solution.	Dens. Change for ± 1°.
1·01	2·14	22	·00016	**1·11**	21·9	243	·00043
1·02	4·13	42	·00019	**1·12**	23·8	267	·00045
1·03	6·15	64	·00021	**1·13**	25·7	291	·00048
1·04	8·16	85	·00024	**1·14**	27·7	315	·00050
1·05	10·17	107	·00027	**1·15**	29·6	340	·00052
1·06	12·19	129	·00040	**1·16**	31·5	366	·00054
1·07	14·17	152	·00032	**1·17**	33·5	392	·00056
1·08	16·15	174	·00035	**1·18**	35·4	418	·00058
1·09	8·11	197	·00038	**1·19**	37·2	443	·00059
1·10	20·0	220	·00040	**1·20**	39·1	469	·00060

DENSITY OF NITRIC ACID, $HNO_3 . Aq$

Grammes per c.c. at 15° C. % N_2O_5 = ·857 × % HNO_3—by weight. (Lunge and Rey, 1891.)

Dens.	Grammes HNO_3 in 100 gm. of Solution.	Grammes HNO_3 in 1 litre of Solution.	Dens. Change for ± 1°.	Dens.	Grammes HNO_3 in 100 gm. of Solution.	Grammes HNO_3 in 1 litre of Solution.	Dens. Change for ± 1°.
1·02	3·70	38	·00022	**1·32**	50·7	669	·00109
1·04	7·26	75	·00028	**1·34**	54·1	725	·00114
1·06	10·7	113	·00034	**1·36**	57·6	783	·00120
1·08	13·9	151	·00040	**1·38**	61·3	846	·00126
1·10	17·1	188	·00045	**1·40**	65·3	914	·00132
1·12	20·2	227	·00051	**1·42**	69·8	991	·00137
1·14	23·3	266	·00057	**1·44**	74·7	1075	·00143
1·16	26·4	306	·00062	**1·46**	80·0	1168	·00149
1·18	29·4	347	·00068	**1·48**	86·0	1274	·00154
1·20	32·4	388	·00074	**1·50**	94·1	1411	·00160
1·22	35·3	430	·00080	**1·504**	96·0	1444	·00161
1·24	38·3	475	·00086	**1·508**	97·5	1470	·00162
1·26	41·3	521	·00091	**1·512**	98·5	1490	·00163
1·28	44·4	568	·00097	**1·516**	99·2	1504	·00164
1·30	47·5	617	·00103	**1·520**	99·7	1515	·00166

DENSITY OF SULPHURIC ACID, $H_2SO_4 \cdot Aq$

Grammes per c.c. at 15° C. % SO_3 = ·816 × % H_2SO_4—by weight.
(Lunge and Isler, 1895.)

Density.	Grammes H_2SO_4 in 100 gm. of Solution.	Grammes H_2SO_4 in 1 litre of Solution.	Density.	Grammes H_2SO_4 in 100 gm. of Solution.	Grammes H_2SO_4 in 1 litre of Solution.
1·02	3·03	31	1·64	72·0	1181
1·04	5·96	62	1·66	73·6	1222
1·06	8·77	93	1·68	75·4	1267
1·08	11·60	125	1·70	77·2	1312
1·10	14·35	158	1·72	78·9	1357
1·12	17·01	191	1·74	80·7	1404
1·14	19·61	223	1·76	82·4	1451
1·16	22·19	257	1·78	84·5	1504
1·18	24·76	292	1·80	86·9	1564
1·20	27·3	328	1·81	88·3	1598
1·22	29·8	364	1·82	90·0	1639
1·24	32·3	400	1·822	90·4	1647
1·26	34·6	435	1·824	90·8	1656
1·28	36·9	472	1·826	91·2	1666
1·30	39·2	510	1·828	91·7	1676
1·32	41·5	548	1·830	92·1	1685
1·34	43·7	586	1·832	92·5	1695
1·36	45·9	624	1·834	93·0	1706
1·38	48·0	662	1·836	93·8	1722
1·40	50·1	702	1·838	94·6	1739
1·42	52·1	740	1·840	95·6	1759
1·44	54·1	779			
1·46	56·0	817	1·8405	95·9	1765
1·48	57·8	856	1·8410	97·0	1786
1·50	59·7	896	1·8415	97·7	1799
1·52	61·6	936	1·8410	98·2	1808
1·54	63·4	977	1·8405	98·7	1816
1·56	65·1	1015	1·8400	99·2	1825
1·58	66·7	1054	1·8395	99·4	1830
1·60	68·5	1096	1·8390	99·7	1834
1·62	70·3	1139	1·8385	99·9	1838

PRESSURE OF AQUEOUS VAPOUR

Expressed in millimetres of mercury at 0°, density of mercury = 13·59593 at latitude 45° and at the sea-level.

Calculated from Regnault's measurements by Broch (*Trav. et Mém. du Bur. intern. des Poids et Mes.* I A. 33, 1881).

t	Pressure.	*t*	Pressure.	*t*	Pressure.	*t*	Pressure.
	mm.		mm.		mm.		mm.
−2°·0	3·9499	2°·6	5·5008	7°·1	7·5171	11°·6	10·1614
−1·9	3·9790	2·7	5·5398	7·2	7·5685	11·7	10·2285
−1·8	4·0082	2·8	5·5790	7·3	7·6202	11·8	10·2960
−1·7	4·0376	2·9	5·6185	7·4	7·6722	11·9	10·3639
−1·6	4·0672	3·0	5·6582	7·5	7·7246	12·0	10·4322
−1·5	4·0970			7·6	7·7772		
−1·4	4·1271	3·1	5·6981	7·7	7·8302	12·1	10·5009
−1·3	4·1574	3·2	5·7383	7·8	7·8834	12·2	10·5700
−1·2	4·1878	3·3	5·7788	7·9	7·9370	12·3	10·6394
−1·1	4·2185	3·4	5·8195	8·0	7·9909	12·4	10·7093
		3·5	5·8605			12·5	10·7796
−1·0	4·2493	3·6	5·9017	8·1	8·0452	12·6	10·8503
−0·9	4·2803	3·7	5·9432	8·2	8·0998	12·7	10·9214
−0·8	4·3116	3·8	5·9850	8·3	8·1547	12·8	10·9928
−0·7	3·3430	3·9	6·0270	8·4	8·2099	12·9	11·0647
−0·6	4·3747	4·0	6·0693	8·5	8·2655	13·0	11·1370
−0·5	4·4065			8·6	8·3214		
−0·4	4·4385	4·1	6·1118	8·7	8·3777	13·1	11·2097
−0·3	4·4708	4·2	6·1546	8·8	8·4342	13·2	11·2829
−0·2	4·5032	4·3	6·1977	8·9	8·4911	13·3	11·3564
−0·1	4·5359	4·4	6·2410	9·0	8·5484	13·4	11·4304
		4·5	6·2846			13·5	11·5048
0·0	4·5687	4·6	6·3285			13·6	11·5797
+0·1	4·6017	4·7	6·3727	9·1	8·6061	13·7	11·6550
0·2	4·6350	4·8	6·4171	9·2	8·6641	13·8	11·7307
0·3	4·6685	4·9	6·4618	9·3	8·7224	13·9	11·8069
0·4	4·7022	5·0	6·5067	9·4	8·7810	14·0	11·8835
0·5	4·7361			9·5	8·8400		
0·6	4·7703			9·6	8·8993		
0·7	4·8047	5·1	6·5519	9·7	8·9589	14·1	11·9605
0·8	4·8393	5·2	6·5974	9·8	9·0189	14·2	12·0380
0·9	4·8741	5·3	6·6432	9·9	9·0792	14·3	12·1159
1·0	4·9091	5·4	6·6893	10·0	9·1398	14·4	12·1943
		5·5	6·7357			14·5	12·2731
1·1	4·9443	5·6	6·7824	10·1	9·2009	14·6	12·3523
1·2	4·9798	5·7	6·8293	10·2	9·2623	14·7	12·4320
1·3	5·0155	5·8	6·8765	10·3	9·3241	14·8	12·5122
1·4	5·0515	5·9	6·9240	10·4	9·3863	14·9	12·5928
1·5	5·0877	6·0	6·9718	10·5	9·4488	15·0	12·6739
1·6	5·1240			10·6	9·5117		
1·7	5·1606	6·1	7·0198	10·7	9·5750	15·1	12·7554
1·8	5·1975	6·2	7·0682	10·8	9·6387	15·2	12·8374
1·9	5·2346	6·3	7·1168	10·9	9·7027	15·3	12·9198
2·0	5·2719	6·4	7·1658	11·0	9·7671	15·4	13·0027
		6·5	7·2150			15·5	13·0861
2·1	5·3094	6·6	7·2646	11·1	9·8318	15·6	13·1700
2·2	5·3472	6·7	7·3145	11·2	9·8969	15·7	13·2543
2·3	5·3852	6·8	7·3647	11·3	9·9624	15·8	13·3392
2·4	5·4235	6·9	7·4152	11·4	10·0283	15·9	13·4245
2·5	5·4620	7·0	7·4660	11·5	10·0946	16·0	13·5103

PRESSURE OF AQUEOUS VAPOUR *(continued).*

t	Pressure.	*t*	Pressure.	*t*	Pressure.	*t*	Pressure.
	mm.		mm.		mm.		mm.
16°·1	13·5965	20°·6	18·0176	25°·1	23·6579	29°·6	30·7928
16·2	13·6832	20·7	18·1288	25·2	23·7991	29·7	30·9707
16·3	13·7705	20·8	18·2406	25·3	23·9411	29·8	31·1494
16·4	13·8582	20·9	18·3529	25·4	24·0838	29·9	31·3291
16·5	13·9464	21·0	18·4659	25·5	24·2272	30·0	31·5096
16·6	14·0351			25·6	24·3714		
16·7	14·1243	21·1	18·5795	25·7	24·5164	30·1	31·6910
16·8	14·2141	21·2	18·6937	25·8	24·6620	30·2	31·8734
16·9	14·3043	21·3	18·8085	25·9	24·8084	30·3	32·0567
17·0	14·3950	21·4	18·9240	26·0	24·9556	30·4	32·2410
		21·5	19·0400			30·5	32·4262
17·1	14·4862	21·6	19·1567	26·1	25·1035	30·6	32·6124
17·2	14·5779	21·7	19·2740	26·2	25·2523	30·7	32·7995
17·3	14·6702	21·8	19·3920	26·3	25·4018	30·8	32·9875
17·4	14·7630	21·9	19·5105	26·4	25·5521	30·9	33·1765
17·5	14·8563	22·0	19·6297	26·5	25·7032	31·0	33·3664
17·6	14·9501			26·6	25·8551		
17·7	15·0444	22·1	19·7496	26·7	26·0077	31·1	33·5573
17·8	15·1392	22·2	19·8701	26·8	26·1612	31·2	33·7491
17·9	15·2345	22·3	19·9912	26·9	26·3155	31·3	33·9419
18·0	15·3304	22·4	20·1130	27·0	26·4705	31·4	34·1356
		22·5	20·2355			31·5	34·3303
18·1	15·4268	22·6	20·3586	27·1	26·6263	31·6	34·5259
18·2	15·5237	22·7	20·4824	27·2	26·7830	31·7	34·7225
18·3	15·6212	22·8	20·6068	27·3	26·9405	31·8	34·9201
18·4	15·7192	22·9	20·7319	27·4	27·0987	31·9	35·1186
18·5	15·8178	23·0	20·8576	27·5	27·2578	32·0	35·3181
18·6	15·9169			27·6	27·4177		
18·7	16·0166	23·1	20·9840	27·7	27·5784	32·1	35·5186
18·8	16·1168	23·2	21·1110	27·8	27·7399	32·2	35·7201
18·9	16·2176	23·3	21·2388	27·9	27·9023	32·3	35·9226
19·0	16·3189	23·4	21·3672	28·0	28·0654	32·4	36·1261
		23·5	21·4964			32·5	36·3307
19·1	16·4208	23·6	21·6262	28·1	28·2294	32·6	36·5363
19·2	16·5233	23·7	21·7567	28·2	28·3942	32·7	36·7429
19·3	16·6263	23·8	21·8879	28·3	28·5599	32·8	36·9505
19·4	16·7299	23·9	22·0198	28·4	28·7265	32·9	37·1592
19·5	16·8341	24·0	22·1524	28·5	28·8939	33·0	37·3689
19·6	16·9388			28·6	29·0622		
19·7	17·0441	24·1	22·2857	28·7	29·2313	33·1	37·5796
19·8	17·1499	24·2	22·4196	28·8	29·4013	33·2	37·7914
19·9	17·2563	24·3	22·5543	28·9	29·5722	33·3	38·0042
20·0	17·3632	24·4	22·6898	29·0	29·7439	33·4	38·2180
		24·5	22·8259			33·5	38·4329
20·1	17·4707	24·6	22·9628	29·1	29·9165	33·6	38·6488
20·2	17·5789	24·7	23·1003	29·2	30·0900	33·7	38·8657
20·3	17·6877	24·8	23·2386	29·3	30·2644	33·8	39·0837
20·4	17·7971	24·9	23·3777	29·4	30·4396	33·9	39·3027
20·5	17·9071	25·0	23·5174	29·5	30·6157	34·0	39·5228

FACTORS FOR REDUCTION OF

° C. / mms.	0	1	2	3	4	5	6	7	8	9	10	11
7 40	·974	·970	·967	·963	·960	·956	·953	·949	·946	·943	·939	·936
7 42	·976	·973	·969	·966	·962	·959	·955	·952	·949	·945	·942	·939
7 44	·979	·975	·972	·968	·965	·962	·958	·954	·951	·948	·944	·941
7 46	·981	·978	·974	·971	·967	·964	·960	·957	·954	·950	·947	·944
7 48	·984	·981	·977	·974	·970	·967	·963	·960	·956	·953	·949	·946
7 50	·987	·983	·980	·976	·973	·969	·966	·962	·959	·956	·952	·949
7 52	·989	·986	·982	·979	·975	·972	·968	·965	·961	·958	·954	·951
7 54	·992	·989	·985	·981	·978	·975	·971	·967	·964	·961	·957	·954
7 56	·995	·991	·988	·984	·980	·977	·973	·970	·966	·963	·960	·956
7 58	·997	·994	·990	·987	·983	·980	·976	·972	·969	·966	·962	·959
7 60	1·000	·996	·993	·990	·986	·982	·979	·975	·972	·968	·965	·961
7 62	1·002	·999	·996	·992	·988	·985	·981	·978	·974	·971	·967	·964
7 64	1·006	1·002	·998	·995	·991	·987	·984	·981	·977	·973	·970	·966
7 66	1·008	1·004	1·001	·997	·993	·990	·986	·983	·979	·976	·972	·969
7 68	1·010	1·007	1·003	1·000	·996	·993	·989	·985	·982	·979	·975	·972
7 70	1·014	1·009	1·006	1·002	1·998	·995	·991	·988	·984	·981	·977	·974
7 72	1·016	1·012	1·009	1·005	1·001	·998	·994	·990	·987	·983	·980	·977
7 74	1·018	1·015	1·011	1·007	1·003	1·000	·996	·993	·989	·986	·982	·979
7 76	1·021	1·017	1·014	1·010	1·007	1·003	·999	·996	·992	·989	·985	·982
7 78	1·023	1·020	1·016	1·013	1·009	1·006	1·002	·998	·995	·991	·988	·984
7 80	1·027	1·023	1·019	1·015	1·012	1·008	1·004	1·001	·997	·994	·990	·987

N.B.—The volume of a gas measured saturated with water-

GASEOUS VOLUMES TO N.T.P.

12	13	14	15	16	17	18	19	20	21	22	23	24	25
·933	·929	·926	·923	·920	·917	·914	·911	·907	·904	·901	·898	·895	·892
·935	·931	·929	·925	·922	·919	·916	·913	·910	·907	·904	·901	·898	·895
·938	·934	·931	·928	·925	·922	·919	·916	·912	·909	·906	·903	·900	·897
·940	·936	·934	·930	·927	·924	·921	·918	·915	·912	·909	·905	·902	·899
·943	·939	·936	·933	·930	·927	·924	·920	·917	·914	·911	·908	·905	·902
·946	·941	·939	·936	·932	·929	·926	·923	·920	·917	·914	·910	·907	·904
·948	·944	·941	·938	·935	·932	·928	·925	·922	·919	·916	·913	·910	·907
·951	·946	·944	·941	·937	·934	·931	·928	·925	·922	·918	·915	·912	·909
·953	·949	·946	·943	·940	·937	·933	·930	·927	·924	·921	·918	·914	·912
·956	·951	·949	·946	·942	·939	·936	·933	·930	·927	·923	·920	·917	·914
·958	·954	·951	·948	·945	·942	·938	·935	·932	·929	·926	·923	·919	·916
·961	·957	·954	·951	·947	·944	·941	·938	·935	·931	·928	·925	·922	·919
·963	·959	·956	·953	·950	·947	·943	·940	·937	·934	·931	·927	·924	·921
·966	·961	·959	·955	·952	·949	·946	·943	·939	·936	·933	·930	·927	·924
·968	·964	·961	·958	·955	·952	·948	·945	·942	·939	·936	·932	·929	·926
·971	·966	·964	·960	·957	·954	·951	·947	·944	·941	·938	·935	·931	·929
·973	·969	·966	·963	·960	·957	·953	·950	·946	·944	·940	·937	·934	·931
·976	·971	·969	·965	·962	·959	·956	·952	·949	·946	·943	·939	·936	·933
·978	·974	·971	·968	·965	·962	·958	·955	·952	·949	·945	·942	·939	·936
·981	·977	·974	·970	·967	·964	·961	·957	·954	·951	·948	·944	·941	·938
·983	·979	·976	·973	·970	·966	·963	·960	·957	·953	·950	·947	·944	·941

vapour at 15° C. is 1·073 times the (dry) volume at N.T.P.

TABLE FOR CALCULATING THE CALORIFIC VALUE CALORIMETRIC

Scale when burning

C.c. Water. / ° C. Rise.		2200 1100	2180 1090	2160 1080	2140 1070	2120 1060	2100 1050	2080 1040	2060 1030	2040 1020	2020 1010
4·5	9·0	393	389	386	382	379	375	372	368	364	361
4·6	9·2	402	398	394	391	387	384	380	376	373	369
4·7	9·4	410	406	403	399	396	392	387	384	381	377
4·8	9·6	419	415	412	408	404	400	396	393	389	385
4·9	9·8	428	424	420	416	412	409	405	401	397	393
5·0	10·0	437	433	429	425	421	417	413	409	405	401
5·1	10·2	445	441	437	433	429	425	421	417	413	409
5·2	10·4	454	450	446	442	438	434	429	425	421	417
5·3	10·6	463	459	454	450	446	442	438	433	429	425
5·4	10·8	471	468	463	459	454	450	446	442	437	433
5·5	11·0	480	476	472	467	463	459	454	450	445	441
5·6	11·2	489	485	480	476	471	467	462	458	454	449
5·7	11·4	499	494	489	484	480	476	471	466	462	457
5·8	11·6	507	502	497	493	488	484	479	474	470	465
5·9	11·8	515	511	506	501	497	492	487	483	478	473
6·0	12·0	524	519	514	510	505	500	495	491	486	481
6·1	12·2	533	528	523	518	513	509	504	499	494	489
6·2	12·4	542	537	532	527	522	517	512	507	502	497
6·3	12·6	550	545	540	535	530	525	520	515	510	505
6·4	12·8	559	554	549	544	539	534	529	523	518	513
6·5	13·0	568	561	557	552	547	542	538	532	526	521
6·6	13·2	576	571	566	561	555	550	545	540	534	529
6·7	13·4	585	580	575	569	564	559	553	543	542	537
6·8	13·6	594	588	583	578	572	567	562	556	551	545
6·9	13·8	603	597	592	586	581	575	570	564	559	553
7·0	14·0	611	606	600	595	589	588	578	572	567	561
7·1	14·2	620	614	609	603	598	592	586	581	575	569
7·2	14·4	629	623	617	612	606	600	595	589	583	577
7·3	14·6	638	632	626	620	614	609	603	597	591	585
7·4	14·8	646	640	635	629	623	617	611	605	599	593
7·5	15·0	655	649	643	637	631	625	619	613	607	601
7·6	15·2	664	658	652	646	640	634	628	622	616	610
7·7	15·4	673	666	660	654	648	642	636	630	624	618
7·8	15·6	681	675	669	663	656	650	644	638	632	626
7·9	15·8	690	684	677	671	665	659	652	646	640	634
8·0	16·0	699	692	686	680	673	667	661	654	648	642
8·1	16·2	707	701	695	687	682	675	669	662	656	650
8·2	16·4	716	710	703	697	690	684	677	671	664	658
8·3	16·6	725	718	712	705	699	692	685	679	672	666
8·4	16·8	734	727	720	714	707	700	694	687	680	674
° C. Rise / C.c. water.		917 1833	908 1817	900 1800	892 1783	883 1767	875 1750	867 1733	858 1717	850 1700	842 1683

Scale when burning

OF 'A' GAS, IN B.TH.U. PER CUBIC FOOT, FROM THE OBSERVATIONS

$\frac{1}{10}$ cubic foot.

2000 1000	1980 990	1960 980	1940 970	1920 960	1900 950	1880 940	1860 930	1840 920	1820 910	1800 900
357	354	350	346	343	339	336	332	329	325	322
365	362	358	354	351	347	343	340	335	332	329
373	369	366	362	358	355	351	347	343	340	336
381	377	373	370	366	362	358	354	351	347	343
389	385	381	377	373	370	366	362	358	354	350
397	393	389	385	381	377	373	369	365	361	357
405	401	397	393	389	384	380	376	372	368	364
413	409	405	400	396	392	388	384	380	376	371
421	417	412	408	404	400	395	391	387	383	378
429	424	420	416	412	407	403	399	394	390	385
437	432	428	424	419	415	410	406	402	397	393
445	440	436	431	427	422	418	414	409	405	400
453	448	444	439	434	430	425	421	416	412	407
460	456	451	447	442	437	433	428	424	419	414
468	464	459	454	450	445	440	436	431	426	422
476	472	467	462	457	453	448	445	438	434	429
484	479	475	470	465	460	455	450	446	441	436
492	487	482	478	473	468	463	458	453	448	443
500	495	490	485	480	475	470	465	460	455	450
508	503	498	493	488	483	478	473	468	462	457
516	511	506	501	495	490	485	480	475	470	464
524	519	514	508	503	498	492	487	482	477	471
532	527	521	516	511	505	500	495	489	484	479
540	535	529	524	518	513	508	502	497	491	486
548	542	537	531	526	520	515	510	504	499	493
556	530	545	539	534	528	522	517	511	506	500
564	558	552	547	541	535	530	524	519	513	507
572	566	560	555	549	543	537	532	526	520	515
580	574	568	562	556	551	545	539	533	527	522
588	582	576	570	564	558	552	546	541	537	529
596	590	584	578	572	566	560	554	548	542	536
604	597	591	585	579	573	567	561	555	549	543
611	605	599	593	587	581	575	569	562	556	550
619	613	607	601	595	588	582	576	570	564	557
627	621	615	608	602	596	590	583	577	571	565
635	629	622	616	610	603	597	591	584	578	572
643	637	630	624	617	611	605	598	592	585	579
651	645	638	632	625	619	612	606	599	592	586
659	652	646	639	633	626	619	613	606	600	593
667	660	654	647	640	634	627	620	614	607	600
833 1667	825 1650	817 1633	808 1617	800 1600	792 1583	783 1567	775 1550	767 1533	758 1517	750 1500

$\frac{1}{12}$ cubic foot.

DENSITY OF AMMONIA, NH_4HO . Aq

Grammes per c.c. at 15° C.

Dens.	Grams NH_3 in 100 gm. of Solution.	Grams NH_3 in 1 litre of Solution.	Dens. Change for + 1°.	Dens.	Grams NH_3 in 100 gm. of Solution.	Grams NH_3 in 1 litre of Solution.	Dens. Change for + 1°.
·996	·91	9·1	·00019	**·936**	16·82	157·9	·00041
·992	1·84	18·2	·00020	**·932**	18·03	168·1	·00042
·988	2·80	27·7	·00021	**·928**	19·25	178·6	·00043
·984	3·80	37·4	·00022	**·924**	20·49	189·3	·00045
·980	4·80	47·0	·00023	**·920**	21·75	200·1	·00047
·976	5·80	56·6	·00024	**·916**	23·03	210·9	·00047
·972	6·80	66·1	·00025	**·912**	24·33	221·9	·00051
·968	7·82	75·7	·00026	**·908**	25·65	232·9	·00053
·964	8·84	85·2	·00027	**·904**	26·98	243·9	·00055
·960	9·91	95·1	·00029	**·900**	28·33	255·0	·00057
·956	11·03	105·4	·00031	**·896**	29·69	266·0	·00059
·952	12·17	115·9	·00033	**·892**	31·05	277·0	·00060
·948	13·31	126·2	·00035	**·888**	32·50	288·6	·00062
·944	14·46	136·5	·00037	**·884**	34·10	301·4	·00064
·940	15·63	146·9	·00039	**·880**	35·70	314·2	·00066

DENSITY OF SODIUM HYDROXIDE, NaHO . Aq

Grammes per c.c. at 18° C. The percentages indicate grammes of NaOH in 100 grammes of solution. (Bousfield and Lowry, 1905.)

%	Density.	%	Density.	%	Density.	%	Density.
0	·9986	**13**	1·1429	**26**	1·2860	**39**	1·4215
1	1·0100	**14**	1·1540	**27**	1·2968	**40**	1·4314
2	1·0213	**15**	1·1650	**28**	1·3076	**41**	1·4411
3	1·0324	**16**	1·1761	**29**	1·3184	**42**	1·4508
4	1·0435	**17**	1·1871	**30**	1·3290	**43**	1·4604
5	1·0545	**18**	1·1982	**31**	1·3396	**44**	1·4699
6	1·0656	**19**	1·2092	**32**	1·3502	**45**	1·4794
7	1·0766	**20**	1·2202	**33**	1·3605	**46**	1·4890
8	1·0877	**21**	1·2312	**34**	1·3708	**47**	1·4985
9	1·0987	**22**	1·2422	**35**	1·3811	**48**	1·5080
10	1·1098	**23**	1·2532	**36**	1·3913	**49**	1·5174
11	1·1208	**24**	1·2641	**37**	1·4014		
12	1·1319	**25**	1·2751	**38**	1·4115		

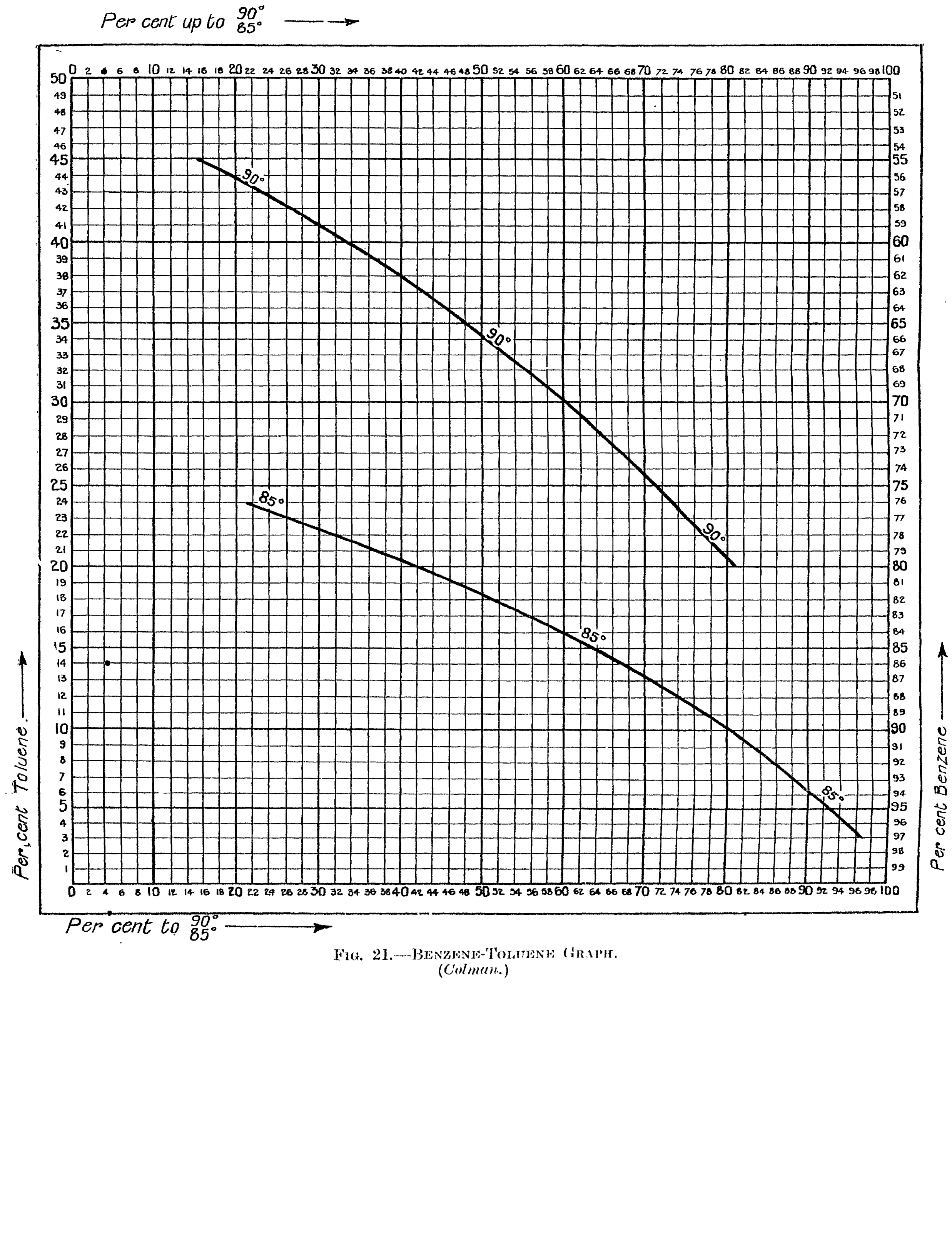

FIG. 21.—BENZENE-TOLUENE GRAPH.
(*Colman.*)

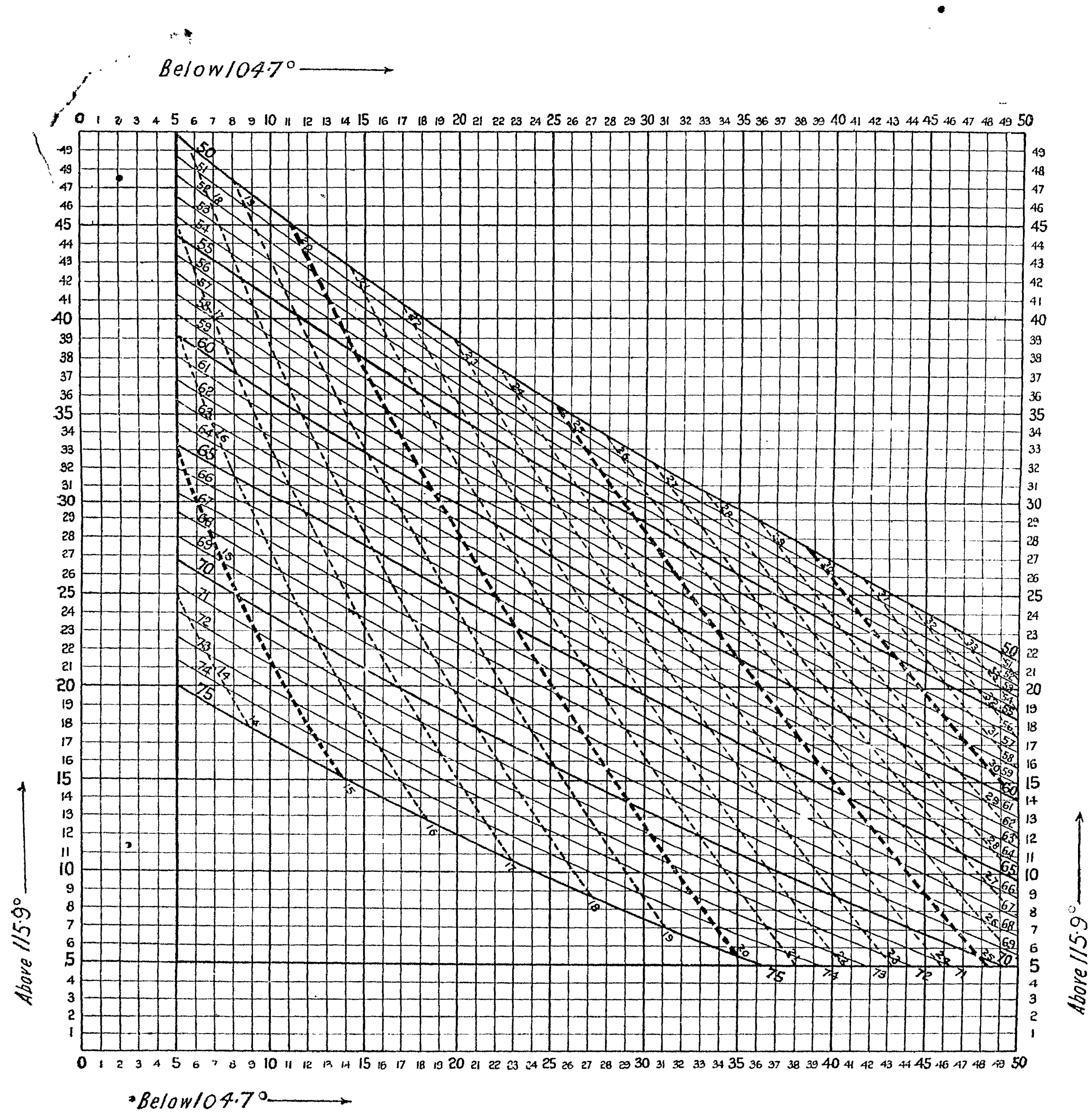

FIG. 22.—BENZENE-TOLUENE-XYLENE GRAPH.
(*Colman.*)

Benzene curves - - - - - - -
Toluene curves ——— ———

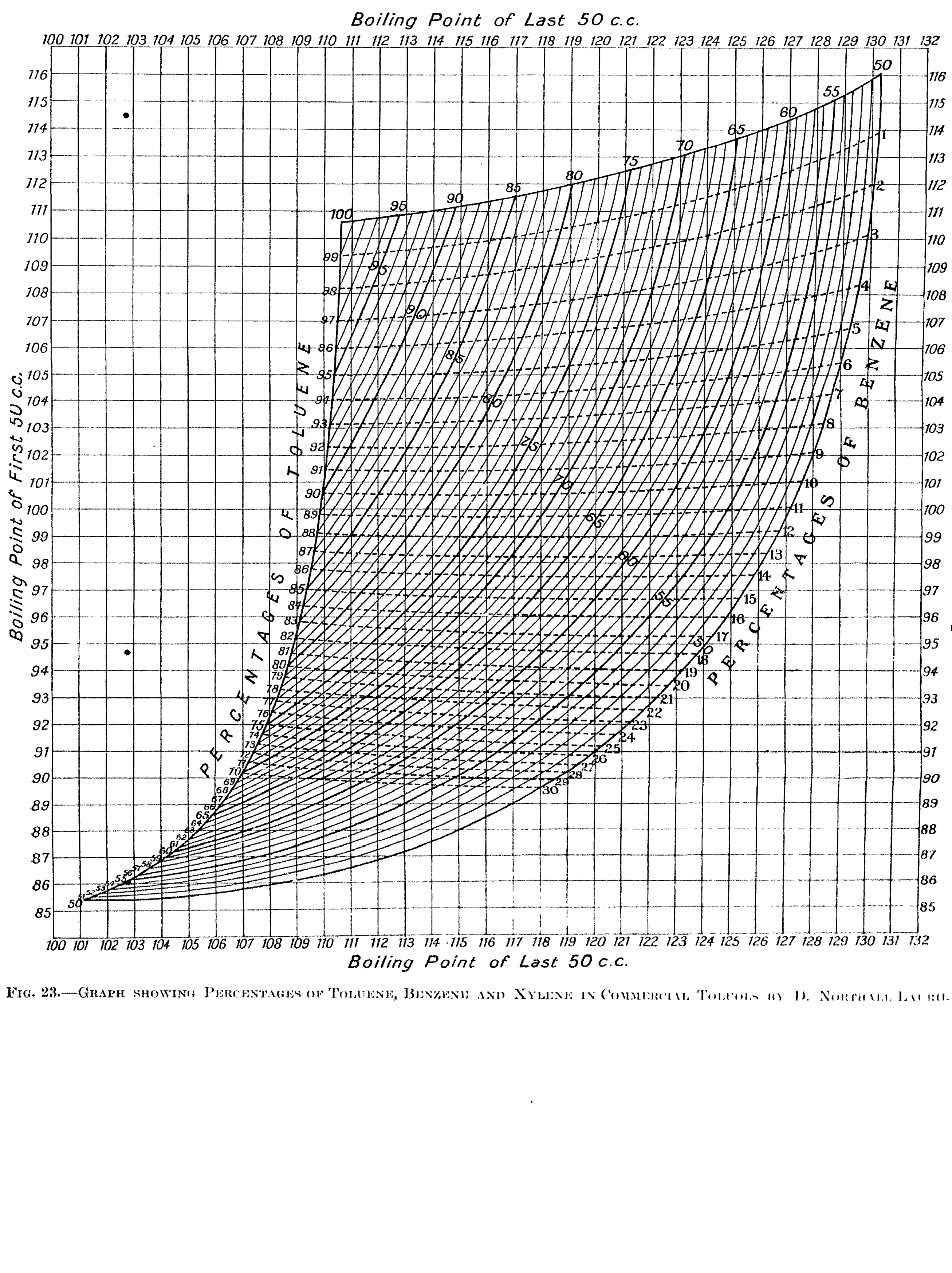

FIG. 23.—GRAPH SHOWING PERCENTAGES OF TOLUENE, BENZENE AND XYLENE IN COMMERCIAL TOLUOLS BY D. NORTHALL LAURIE.

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